# NOTES

ON

METALLURGICAL ANALYSIS.

ARRANGED FOR STUDENTS IN METALLURGICAL CHEMISTRY

Selected Methods for the Analysis of Iron and Steel and of the Materials
used in their Manufacture, Including the Analysis of Gases, Fuels,
Water for Boiler Supply, etc. Together with Explanatory Notes
on the Manipulation and Chemistry of the Various Processes.

BY

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SECOND EDITION REWRITTEN AND GREATLY ENLARGED

PREFACE TO THE FIRST EDITION.

These notes were written for the use of the writer's students in the metallurgical laboratory of the Ohio State University.

The object was to give in a condensed form the series of selected methods in metallurgical analysis which made up the course of study.

To the descriptions of the processes, such explanations have been added as experience has shown to be desirable for the assistance of the student in understanding the conditions necessary for accurate results.

Such methods only are given as have been tested by repeated use in the laboratory and found satisfactory.

No attempt is made to describe general reagents or apparatus, as students prepared to take this course are always familiar with all ordinary laboratory equipment and for special forms of apparatus reference is made to easily accessible books and papers.

The writer wishes to acknowledge his obligation to Blair, Troilius and other standard writers, as well as to numerous papers in the various technical and scientific journals, though it has been impossible to give credit in detail to all the sources from which material was taken in compiling these notes.

The references added are only those which it seemed important the student should consult for fuller information on the subject.

October 28, 1893.

PREFACE TO THE SECOND EDITION.

In preparing the present edition of this book the writer has endeavored to extend its scope and make it not only a text book for students in technical schools but also a book of reference for young men in metallurgical laboratories. With this object the book has been enlarged so as to include methods for the determination of all the elements likely to be encountered in the ordinary work of the laboratory. The subjects of gas analysis and the testing of fuel have been treated at much greater length. To the standard processes given in the first edition such recent ones have been added as have proved to be of general application and value. The descriptions of the processes have been largely re-written and the notes extended and as far as possible brought up to the present state of the science.

To the descriptions of special forms of apparatus cuts have been added. These generally show simple arrangements which have been found by the writer to be well adapted to the use of students and not to require expensive material.

The writer wishes to acknowledge his great obligation to his associates, Professors Wm. McPherson and W. E. Henderson for their assistance in the reading of the proof and for valuable suggestions, and especially to Mr. E. E. Somermeier, Instructor in Metallurgy, to whom he is indebted not only for assistance in revising the manuscript and reading the proof, but also for working up in the laboratory many of the details in the descriptions of the processes.

January 31, 1903.

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INTRODUCTION.

Before begining the course in special analysis given in these notes, the student is supposed to be familiar with the ordinary qualitative reactions of the acids and bases, the preparation of reagents, and so much of the general methods of quantitative analysis as includes the use of the balance and weights, the ordinary operations of filtration, washing, drying, igniting, and weighing of precipitates, the evaporation of solutions, and also the use and calibration of graduated glassware.

A careful study of the first two sections of Fresenius' System of Quantitative Analysis is advisable in regard to all these points of manipulation.

In addition to the above a few general precautions and explanations are necessary and should never be overlooked.

In adding reagents to produce any given effect it is important that the right amount be used. What this will be demands a thorough knowledge of what is to take place. In the descriptions of the various processes these amounts are approximately indicated, but it is impossible to provide in this way for all contingencies. Therefore, if the amount of reagent directed fails to do the work it must be increased or diminished as may appear necessary. Thus in every case where a precipitate is formed, it is *essential* that the filtrate be tested by a further addition of the reagent to make sure that the precipitation is complete. This is best done by adding the reagent to a small portion of the liquid in a test tube, and if a precipitate forms returning this to the main volume; often a little of the clear liquid over the precipitate can be tested in this way before filtration.

The purity of the reagents, even if marked "c.p.", should always be tested. In many cases it is necessary to run a "blank" determination by going through the process with the reagents alone, leaving out the substance to be tested. The amount of any impurity which would affect the result can be thus determined and allowed for.

A process should be tested by repeated determinations made on different amounts of the substance. Agreement of the results in this case is a better indication af accuracy than where the same amounts are taken in each determination.

The amounts of material prescribed in the descriptions of the processes are those most generally used. They may be changed provided the amounts of the reagents be varied to correspond.

In many of the processes the calculations may be greatly simplified by taking "factor weights" of the material instead of even grams.

This consists in weighing out an amount of the substance equal to the fraction that the material to be determined forms of the precipitate weighed. When this is done the weight of the precipitate in grams multiplied by 100 will give directly the percentage sought. If the factor weight is inconveniently large or small some simple multiple of it can be taken and the result estimated accordingly.

For example: $BaSO_4$ contains 0.137 S and if ten times this factor (1.37 grams) of any substance is taken for the determination of sulphur each milligram of $BaSO_4$ obtained represents 0.01 per cent. of sulphur.

A table of convenient factors of this kind is added at the end of this book and the weights there given may be used, when desirable, in place of those directed in the processes.

A similar method is often used in weighing out for volumetric determinations when a standard solution is used of which the value of 1.c.c. is determined experimentally and is not an aloquoit part of a gram. For illustration see directions for the volumetric determination of lime, page 23.

NOTES

ON

METALLURGICAL ANALYSIS.

THE OBTAINING AND PREPARING OF SAMPLES FOR ANALYSIS.

The object sought by the technical analyst is to ascertain the average composition of some particular lot of material — for example, a carload of ore, an ingot of metal or a bin full of coal.

The amount of material treated in the laboratory is of necessity limited to a few grams.

The preparation of this small portion so that its analysis shall correctly represent the composition of the mass from which it is taken, constitutes the operation of "*sampling.*"

The general mode of procedure is to take from the mass in question several portions selected from different points, and containing coarse and fine material in as nearly as possible the same proportion as they exist in the mass as a whole. This large sample which may weigh from 200 pounds to a ton, according to the amount of material the chemist has to examine, as well as to the *extent of variation permissible in the results*, is then crushed to one-half inch or

smaller, thoroughly mixed and subdivided by "quartering," until a sample of about ten pounds is obtained. This is pulverized and all put through a 6 mesh sieve, well mixed and again subdivided, till a sample of 100 to 200 grams is obtained, which is put through an 80 to 100 mesh sieve and bottled for use.

The operation of "quartering" is conducted as follows. The material after being well mixed by shoveling is formed into a pile which is then flattened out by a spiral motion of the shovel. This pile is then divided into four quarters by cutting across at right angles.

Two diagonally opposite quarters are selected and the intermediate ones removed. Care should be taken to brush away carefully all the material of the rejected quarters.

The two remaining ones are then mixed together and the operation repeated until a sufficient reduction in bulk is made.

Many variations from this general procedure will be necessary with different materials. The following general principles may be stated as a guide:

1. As to the size of the original large sample. This must be greater as the material is less homogeneous and as the importance of the exact determination of any ingredient increases. Thus, a limestone can be easily sampled; but a gold or silver ore consisting of small, detached fragments of a very valuable material in a valueless rock may require the fine crushing of the whole mass of ore and its careful mixing and subdivision, to secure an "average assay."

2. Materials of decidedly different specific gravities require great care to prevent separation into layers during mixing. (Quartering constitutes a fair safeguard against this source of error.)

3. When the ore is sifted, every particle must go through the sieve. The harder parts which are left unbroken till the last, are often of different composition from the softer and first pulverized portions, and if rejected would cause serious error.

4. Certain ores and slags contain particles of metal which can not be pulverized. In this case the grains of metal not passing

through the sieve must be collected and weighed. The portion passing through the sieve is also weighed. The metal and the siftings are then analyzed separately, and the two analyses combined in the ratio of the relative weights.

The sampling of metals presents many difficulties. Melted metals can be sampled during pouring by taking a little at the beginning, middle and end of the cast, and averaging the three analyses.

In general it may be stated—

1. Cast ingots are *not* homogeneous. Drilling from different portions will show different analyses. Hence, drillings from a number of points must be well mixed. A single "pig" of cast iron may vary largely in composition from top to bottom.

2. In tapping a mass of metal from a furnace, different portions of the "run" will show differences in composition. Thus, a "bed" of pig iron will show wide variations in silicon and sulphur between the top and bottom of the cast.

3. In some metals the operation of drilling will result in a separation; for example, in drilling pig iron, the fine portion will be of different composition from the coarse; hence, careful mixing of the drillings is necessary.

SAMPLING APPARATUS.

For hand sampling, a laboratory should be equipped with a small jaw crusher, a "bucking plate" of heavy cast iron, a couple of iron mortars, a steel mortar, an anvil, a couple of stone hammers and a sledge, and several zinc trays and tin cake dishes for holding samples. Sieves are best made of brass wire and should be provided with tight bottoms and covers. Dust is easily lost in sifting and is likely to be of different composition from the rest of the sample.

A disc of brass or iron such as an old two-ounce weight

put into the sieve greatly assists the work on the finer sieves by preventing "caking" of the fine material in the sieve.

For sieves of ¼-inch and over, iron netting put on wooden frames may be used.

A wooden or cement floor is desirable for quartering large samples, but rubber or oil cloth spread out on the ground can be used.

It should never be forgotten that in grinding hard material with metallic apparatus more or less of the metal will go into the product. Thus, a sample of blast furnace slag ground down in an iron mortar would show more iron than was actually in the slag, therefore for the accurate determination of a small amount of iron in such a material a special sample crushed in agate should be prepared.

For sampling metals a drill is desirable. This must be worked *dry* (without oil) and care should be taken to reject the outer "skin" of the ingot or bar, which is usually contaminated with matter not properly belonging in the analysis. Cast iron is frequently sampled by pouring a little of the molten metal into water. This makes the iron white and very brittle. These so called "shot samples" and similar brittle material as "spiegel iron" and "wash metal" which are too hard to drill, must be broken into small fragments with a sledge hammer and several pieces pulverized in a steel mortar. A very efficient mortar for this purpose can be made by boring a hole two inches deep and one inch in diameter into a block of tool steel about three inches square and four inches high. Fit this with a steel "rammer" cut from a round bar and about three inches longer than the hole. It must be only slightly smaller than the hole in the block. Both block and rammer must be well hardened. By dropping a fragment of metal into the hole, inserting the rammer and pounding it vigorously with a heavy hammer the hardest material is soon reduced to a fine sand.

Sampling by machinery is necessary where large amounts of ore are handled. For descriptions, of sampling plants see the references p. 13.

"WEIGHING OUT" FROM THE LABORATORY SAMPLE.

In this operation the tendency of materials of different specific gravity to separate must never be lost sight of. The substance should be carefully mixed upon a sheet of glazed paper and small portions taken from different parts.

A second source of error is the separation of coarse and fine, as in metal drillings. Great care is necessary to avoid serious difficulty here. The drillings may be moistened with alcohol to make them adherent, and then small portions may be separated, to be subsequently accurately weighed when dry (Shimer).

Dirty pig iron samples are frequently sent to the chemist, the drillings being contaminated by sand, wood, grease, etc. These may be cleaned from sand with a magnet and from grease by washing with ether, but the analytical results on such samples should never be regarded as entirely satisfactory.

References on sampling — machinery and methods—

A. A. Blair—The Chemical Analysis of Iron,
Jour. An. and App. Chem., vol. V, p. 299—sampling iron ores.
Jour. An. and App. Chem., vol. II, p. 148—as to irregularity of pig iron.
Eng. and Min. Jour., 1892, p. 75—sampling machine.
Trans. Inst. Min. Engs., vol. XIV, p. 760, P. W. Shimer, sampling cast iron borings.
Trans. Inst. Min. Engs., vol. XX, p. 155, Wm. Glenn, sampling ores.
Trans. Inst. Min. Eng., vol. XX, p. 416, H. L Benjamin, sampling machine, and also illustration of hand sampling.
Trans. Inst. Min. Engs., vol. XX, p. 611, E. K. Landis, iron ore sampling.
Eng. and Min. Jour., vol. 71, p. 534.
Jour. Soc. Chem. Ind., 1898, p. 123.

ESTIMATION OF MOISTURE.

Many materials (ores, clays, limestones, etc.) as sampled in bulk are often too damp to pulverize. Such samples must be dried in a steam bath or by other means, and the loss of weight determined. This drying can be done on a portion (one or two pounds or more) of the crushed and mixed material, which, after drying, is pulverized for

the final sample. It is also always well to determine moisture in the final sample, and allow for it if present. The temperature for drying must not exceed 100° C, or water of composition may be expelled.

The analysis may be stated on the "dry basis," but should also be calculated on the basis of the wet material.

For example. A cargo of iron ore was sampled in the vessel while unloading, as follows: After the bottom of the boat was reached, portions of the ore were taken every 18 inches from the top to the bottom of the sloping sides of the ore exposed in the hold, including lump and fine in the proportions they formed at each point. This was repeated when the vessel was about half unloaded. The total amount taken was 200 pounds. This was broken up as fine as beans, well mixed by shoveling and divided by quartering until a portion of two pounds was obtained, all being done rapidly to avoid loss of moisture.

This portion was weighed on an ore scales.

Weight...........................	925.4 grms.
After drying in a pan on a steam boiler—weight.................	864.9 grms.
Loss...........................	60.5 grms.

This was then pulverized and mixed, and a portion of 100 grms. taken for the laboratory. This assayed—

Iron........................... 58.4 per cent.

Then 925.4 : 864.9 = 58.4 : 54.6 = the per cent. of iron in the ore in its original condition.

It may be noted 1st, that many ores will absorb water during the pulverization. The amount of water so absorbed will vary with the weather; 2d, complete drying of a large sample is very difficult; 3d, ordinary corked bottles are not moisture proof, and samples left in such will change in the course of time, if they are hygroscopic.

In the case of coal, especially the "dry" or non coking coals and lignites, sampling so as to preserve the moisture in the material

unaltered presents many difficulties. Such coals when pulverized, rapidly lose moisture in dry air at ordinary temperatures, and if then exposed to moist air partially regain it.

The original sample should be rapidly crushed and quartered down, avoiding all unnecessary exposure to air. The final sample can be preserved in rubber sealed "fruit jars."

In preparing the small fine sample for analysis, speed and covered sieves are necessary. The pulverized material must be kept in bottles with rubber corks.

Wet samples, such as coal from a "washer," may be air dried at room temperatures until they can be pulverized, but will not then show, as a rule, the same moisture as the original coal before wetting; hence, if this coal is to be compared with the coal before washing, that should be similarly air dried.

Where much work is done special ovens for drying samples are of great assistance. For description of one used at the Edgar-Thomson Steel Works, see Blair, The Chemical Analysis of Iron.

THE ANALYSIS OF LIMESTONES.

The constituents to be determined are the insoluble silicious matter, oxide of iron and alumina, carbonate of lime and carbonate of magnesia. The silicious matter consists of sand (silica) and silicates chiefly clay (silicate of alumina). The iron is sometimes present as ferrous carbonate. Small traces of phosphoric acid and sulphates are also often present; they are not considered in this place, but can be determined as in iron ores.

In examining limestone quarries to determine the quality of the stone for furnace flux, lime or cement manufacture, the rock should be sampled layer by layer, as different layers usually vary greatly from each other in composition, while material from the same layer (or "bed") is likely to be of moderately uniform composition. The stone generally ranks in quality according to the amount of carbonate of lime.

Process of Analysis.— Weigh 1 grm. of the finely ground sample. Transfer it to a 4-in. casserole or dish, cover with a watch glass, add 25 to 30 c.c. of water, then 15 c.c. of concentrated HCl, and warm until all effervescence has ceased. Remove the cover, wash it off into the dish, add 4 or 5 drops of HNO_3 and evaporate the solution to dryness on a water bath or hot plate; or replace the cover and boil down directly over the lamp, using constant care to prevent loss by "spattering;" finally heat very carefully over the lamp flame until all odor of HCl is gone. The temperature attained should not exceed 120° C. It can be regulated by drying in an air bath, but the "trick" of doing it as indicated is soon learned and saves much time. Now cool, add 5 c.c. of HCl, warm till the Fe salts are dissolved, add 50 c.c. of water and heat until everything dissolves except the silicious matter, which forms a flocculent or sandy residue. Filter through a 5 or 7 cm. filter, and wash thoroughly with hot water until a few drops of the washings show no reaction for HCl when tested with $AgNO_3$.

Ignite and weigh the residue, which, after deducting the

weight of the filter ash, constitutes the "insoluble silicious matter." Keep it for the determination of the silica by fusion.

To the filtrate, the volume of which should be about 100 c.c., carefully add NH_4OH until it just smells distinctly of NH_3. Should the precipitate be light colored and large in amount, indicating the probable precipitation of $Mg(OH)_2$, add 5 c.c. HCl and again NH_4OH as before. Now boil the liquid about five minutes or until the odor of NH_3 has nearly gone—maintaining the volume of the liquid if necessary by adding water from time to time. Remove the lamp, and let the precipitate settle, filter into a small filter, wash well with hot water, ignite and weigh the precipitate of $Fe_2O_3 + Al_2O_3 + P_2O_5$.

The Fe_2O_3 and P_2O_5 may be determined in another portion, and when deducted from the above will give the alumina by difference.

Dilute the filtrate to about 200 c.c. If it is not distinctly alkaline add five to ten drops of NH_4OH, heat to boiling and slowly add 80 c.c. of a solution of $(NH_4)_2C_2O_4$ heated to boiling also. Use a saturated solution of the salt diluted with an equal volume of water. Stir well during the addition of the reagent and for a minute or two afterwards, then set aside until the precipitate of CaC_2O_4 has settled completely. Decant the liquid through a 9 cm. filter without disturbing the precipitate, wash the precipitate once or twice by decantation, using about 100 c.c. of boiling water each time, then transfer it to the filter and wash 6 or 7 times with hot water. When the filtrate is to be concentrated for the determination of the magnesia, set aside the first filtrate and decantation and catch the subsequent washings in a separate beaker. Concentrate these by boiling down to a small volume and then add them to the first portion.

Dry the precipitate thoroughly, detach it as far as possible from the filter, put it in a weighed No. 0 porcelain

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Ignite and weigh the residue, which, after deducting the

weight of the filter ash, constitutes the "insoluble silicious matter." Keep it for the determination of the silica by fusion.

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The Fe_2O_3 and P_2O_5 may be determined in another portion, and when deducted from the above will give the alumina by difference.

Dilute the filtrate to about 200 c.c. If it is not distinctly alkaline add five to ten drops of NH_4OH, heat to boiling and slowly add 80 c.c. of a solution of $(NH_4)_2C_2O_4$ heated to boiling also. Use a saturated solution of the salt diluted with an equal volume of water. Stir well during the addition of the reagent and for a minute or two afterwards, then set aside until the precipitate of CaC_2O_4 has settled completely. Decant the liquid through a 9 cm. filter without disturbing the precipitate, wash the precipitate once or twice by decantation, using about 100 c.c. of boiling water each time, then transfer it to the filter and wash 6 or 7 times with hot water. When the filtrate is to be concentrated for the determination of the magnesia, set aside the first filtrate and decantation and catch the subsequent washings in a separate beaker. Concentrate these by boiling down to a small volume and then add them to the first portion.

Dry the precipitate thoroughly, detach it as far as possible from the filter, put it in a weighed No. 0 porcelain crucible, burn the filter carefully on a platinum wire and add

the ash to contents of the crucible. Now drop concentrated H_2SO_4 on to the precipitate till it is well moistened, but avoid much excess. Heat the crucible (working under a "hood" to carry off the fumes) holding the burner in the hand and applying the flame cautiously until the swelling of the mass subsides, and the excess of H_2SO_4 has been driven off as white fumes. Finally heat to a cherry red for 5 minutes. Do not use the blast lamp. Cool and weigh the $CaSO_4$. The weight of the $CaSO_4$ multiplied by 0.735 gives the amount of $CaCO_3$ in the sample. The filtrate from the CaC_2O_4 should be, if over that volume, concentrated by boiling to 300cc; should any MgC_2O_4 separate, dissolve it by adding a little HCl. Cool, add NH_4OH till alkaline, then add 10 c.c. or a sufficient quantity of a saturated solution of Na_2HPO_4. Then add gradually $\frac{1}{10}$ of the volume of the liquid of strong NH_4OH, (sp. gr. 0.90) stir hard for some time, cover and let settle until the liquid is perfectly clear (about 2 hours), filter and wash with water containing $\frac{1}{10}$ of its volume of strong NH_4OH and a little NH_4NO_3. 10 c.c. of the phosphate solution is sufficient for about 20 per cent. of $MgCO_3$; for dolomites more must be added. Dry the precipitate, detach it from the filter and burn the filter on a platinum wire; now ignite precipitate and filter ash in a porcelain crucible, first heating carefully over a Bunsen burner till all volatile matter is driven off and it has been at a dull red heat for some minutes, then finishing over the blast lamp for five or ten minutes.

The ignited precipitate is $Mg_2P_2O_7$, the weight of which multiplied by 0.757 gives the $MgCO_3$ in the sample.

Treatment of the Silicious Residue for the Determination of SiO_2.—Mix the ignited residue with 8 or 10 times its weight of dry Na_2CO_3, in a platinum crucible of at least 15 c.c. capacity, heat it over a Bunsen burner until the mass has well caked together, then over a blast lamp until it is in quiet fusion. Now remove the crucible with a pair of tongs and dip the bottom in cold water, which will usually cause the mass to loosen.

Wash off any of the material spattered on the cover of the crucible into a casserole with hot water. Add the fused cake, if it has come loose; if not, fill the crucible with water and warm until the fused mass softens up and can be transferred to the casserole. Finally clean the crucible with hot water and add the washings. If any material adheres so as not to be removed by washing with water, dissolve it with a little HCl and add to the rest, (on no account punch or dig the material out, as this may ruin the crucible). When the fusion has been thoroughly disintegrated by the hot water and no hard lumps are left, cover the dish and add HCl until everything dissolves, and warm till effervescence ceases. Remove and wash off the cover and evaporate the solution to dryness on a water bath or otherwise; when dry and every trace of odor of HCl has gone, add 10 c.c. dilute HCl (1:1) and then 50 c.c of water. Warm till the Na Cl has dissolved, filter, wash well with hot water, dry and ignite the residual SiO_2. The ignition must be repeated and the residue reweighed until its weight does not change.

In the filtrate the iron, alumina, lime and magnesia may be determined as in the regular process, and the amounts so found added to the weight of the main precipitates.

NOTES ON THE PROCESS.

1. Limestones sometimes contain silicates which are decomposed by treatment with HCl, part of the SiO_2 going into solution This is made insoluble by evaporation to dryness. The presence of $CaCl_2$ renders the dehydration of the SiO_2 easy at the temperature of the water bath. A much higher temperature is to be avoided as silica may recombine with the bases, and so either be redissolved on treatment with acid, or hold bases insoluble.

2. When the amount of residue is considerable it is often necessary to determine the silica it contains. In this case it is rendered soluble by fusion with excess of Na_2CO_3. The addition of $NaNO_3$ is to be avoided, as it becomes caustic and attacks platinum ware. A gram of NaCl is sometimes added to the fusion mixture. It is said to assist the subsequent solution and disintegration of the fused mass. The fused mass, consisting of sodium silicate and aluminate, should be thoroughly soaked in water till it becomes soft and disin-

tegrated, most of the sodium silicate being dissolved; then on adding HCl a clear solution without residue is at once obtained. If the HCl is added to the fused mass before this disintegration, it causes a gelatinous film of hydrated SiO_2 to separate and to enclose the pieces, arresting further action. A single evaporation of the SiO_2 solution even if dried for hours fails to render the SiO_2 completely insoluble, 97 to 98% only being recovered. The SiO_2 is not entirely pure, however, and these errors tend to balance each other. The impurity present is largely alumina, and the trace of SiO_2 dissolved is mostly precipitated with the alumina in the subsequent analysis. In order to obtain the whole of the SiO_2 it is necessary to evaporate the filtrate from the first portion to dryness as before, and weigh the additional SiO_2 thus separated. This is better than a double evaporation of the original solution.

3. The SiO_2 is hard to wash, retaining alkaline salts tenaciously. It must be thoroughly washed with hot water till the filtrate no longer shows a trace of HCl when tested with $AgNO_3$.

4. The SiO_2 must be ignited to *constant weight*, as it retains water most tenaciously. A blast lamp is necessary to remove the last traces.

5. $Fe(OH)_3$ and $Al(OH)_3$ are insoluble in solutions of of NH_4Cl, but a large excess of NH_4OH holds $Al(OH)_3$ in solution to a small extent. This is entirely separated by boiling off the excess of NH_4OH or by the presence of a large excess of NH_4Cl. Too much boiling renders the iron and alumina precipitate slimy and difficult to wash and filter; hence, care is necessary in adding the NH_4OH to avoid large excess, so that a few minutes boiling will be sufficient. When the slimy condition occurs a drop of strong ammonia will sometimes cause it to settle better.

6. $Mg(OH)_2$ is not completely soluble in NH_4OH unless sufficient NH_4Cl be present. It separates as a white precipitate, easily mistaken for alumina, so unless the $Fe(OH)_3 + Al(OH)_3$ precipitate is small in amount it is well to redissolve it in considerable HCl and reprecipitate by NH_4OH. If *much* Fe and Al are present the precipitate will certainly contain CaO and MgO, which must be removed by re-solution and reprecipitation after decantation and partial washing. Solutions containing NH_4OH and CaO will absorb CO_2 on standing, precipitating $CaCO_3$; hence the $Fe(OH)_3 + Al(OH)_3$ must be filtered and washed promptly. On long standing a crystalline precipitate of $CaCO_3$ will sometimes be formed in the beaker with the $Fe(OH)_3 + Al(OH)_3$; of course in this case re-solution and re-precipitation are necessary. Distilled water often contains CO_2 which will cause a precipitation in the same way. Hence, boiling the water before use is recommended. Cold water in a wash bottle

rapidly absorbs CO_2 from the breath; such water should never be used in diluting the alkaline liquid holding the $Fe(OH)_3 + Al(OH)_3$ precipitate.

7. *Calcium Oxalate* is very insoluble, but it is a difficult precipitate to filter and wash if not formed exactly right. On gentle ignition below visible redness it is changed to carbonate, and as such may be weighed; slightly too high a temperature however expels some CO_2. The complete conversion to *oxide* requires a very high temperature for a long time. The action of concentrated H_2SO_4 on calcium oxalate converts it to $CaSO_4$. The action is not violent and the excess of H_2SO_4, provided it is moderate, can be driven off with out danger of loss by spurting. $CaSO_4$ will stand the cherry red heat of a Bunsen burner without alteration, the higher heat of a blast lamp will cause it to lose SO_3.

8. Magnesium will precipitate as oxalate in concentrated solutions, hence when much is present a re-solution of the calcium oxalate in a little dilute HCl after a partial washing may be necessary. This is rarely the case in ordinary limestone, if the calcium is precipitated in properly diluted solutions. In the analysis of dolomites the calcium precipitate must always be redissolved. In this case, after washing the calcium oxalate by decantation once, cautiously add HCl to the precipitate in the beaker until it just dissolves on warming. Dilute to about 100 c.c., add 2 or 3 c.c. of $(NH_4)_2C_2O_4$ solution, then heat to boiling and add while stirring dilute NH_4OH till distinctly alkaline. Allow the precipitate to settle, filter and wash, adding this filtrate to the original one.

9. On concentrating the filtrate from the calcium oxalate, a crystalline precipitate of magnesium oxalate will sometimes separate. This can be redissolved in HCl and added to the solution. If it contains any calcium oxalate it will leave a milky solution clearing slowly.

10. As the liquid in which the magnesium is precipitated contains all the material added in the analysis, careless addition of reagents may give so strong a solution of ammonium and sodium salts that the precipitation of the magnesium phosphate will not take place promptly unless the solution be largely diluted with water and ammonia. From such a volume of liquid the Mg will not wholly come down. In such a case the filtrate should be evaporated to dryness with excess of HNO_3 (3cc for each gram NH_4Cl) which will decompose and remove the ammonium salts (they are broken up into nitrogen and water) and then any remaining magnesium precipitated.

See Crookes "Select Methods of Chemical Analysis."

11. There must be enough $(NH_4)_2C_2O_4$ solution added to convert all the Mg. as well as Ca to oxalate or CaC_2O_4 will not completely precipitate.

12 Sodium oxalate, being very sparingly soluble, will sometimes separate with the Mg. precipitate, especially when the solution is concentrated and much Na_2HPO_4 has been added; in this case, after partial washing, the precipitate must be dissolved in HCl and reprecipitated by NH_4OH.

References—

SiO$_2$ separation, Jour. Anal. and App. Chem. Vol. IV, P. 159.

Mg. Ca. separation, Fresenius, Quantative Analysis, §73; §74; §101; §104; §154.

THE VOLUMETRIC DETERMINATION OF CALCIUM AND MAGNESIUM.

Instead of weighing the precipitate of CaC_2O_4 it may be determined by measuring the volume of a standard solution of $KMnO_4$ required for oxidizing the oxalic acid it contains.

The precipitate is first dissolved in dilute H_2SO_4. The reaction is as follows:

$$5CaC_2O_4 + 8H_2SO_4 + 2KMnO_4 = 5CaSO_4 + K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$
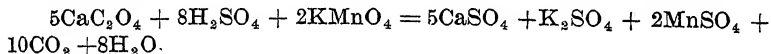
This reaction takes place rapidly at 60° to 70° C. The first few drops of permanganate color the liquid and a few seconds will elapse before this color disappears, then the reagent may be added rapidly. This delay in starting is entirely removed if a few drops of a strong solution of $MnSO_4$ are added to the liquid before titration.

The $MgNH_4PO_4$ precipitate has an alkaline reaction and can be determined volumetrically by measuring the amount of standard acid required to neutralize it. The end reaction is not so clear cut as in the permanganate reaction with CaC_2O_4 but with a little experience is satisfactory. The reaction is as follows:

$$MgNH_4PO_4 + H_2SO_4 = MgSO_4 + NH_4H_2PO_4,$$
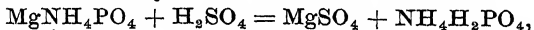
$NH_4H_2PO_4$ being neutral to cochineal solution.

SOLUTIONS REQUIRED.

A.—Standard Potassium Permanganate.

The same solution can be used as for the determination of iron in ores, 1 c.c. of which is equal to 0.01 gram of Fe. 1 c.c. of such a solution is equivalent to 0.008929 gram of $CaCO_3$, in the above reaction.

B.—*Standard Acid.*

One-tenth "normal" H_2SO_4 can be used, 1 c.c. being equivalent to .0042 gram of $MgCO_3$.

C.—*Standard Alkali.*

One-tenth normal ammonia can be used. It is easily prepared and by using cochineal as an indicator is perfectly satisfactory. It has little tendency to absorb CO_2 and its loss of strength by evaporation of ammonia is so slight that it will keep for weeks practically unaltered.

D.—*Tincture of Cochineal.*

Coarsely pulverize 2 or 3 grams of cochineal in a small porcelain mortar, moisten with dilute alcohol (1 vol. alcohol to 3 vols. water) and transfer to a funnel containing a 9 cm. filter paper. When the alcohol has run through wash with successive small portions of 25 per cent. alcohol until about 20-25 c.c. have run through and most of the color is extracted. Now dilute the colored extract with 25 per cent. alcohol to about 100 c.c. for each gram of cochineal taken. This mode of extracting with a small quantity of alcohol avoids the solution of much of the material other than the color. The solution keeps much better than when the whole of the alcohol is used in extracting as is sometimes directed.

PROCESS.

A.—*For Limestones low in Magnesia.*

Weigh out 0.8929 gram of the finely ground sample into a small porcelain or platinum crucible, ignite cautiously to dull redness to destroy organic matter. Transfer the ignited powder to a beaker holding 300 or 400 c.c., add 20 c.c. of water, cover and then add 15 c.c. of HCl and 3 or 4 drops of HNO_3. Boil till all the soluble matter is dissolved and all the CO_2 expelled. Wash off and remove the cover and dilute the liquid to about 150 c.c. with water free from CO_2. Add NH_4OH in slight excess and heat to boiling,

then without filtering, precipitate the CaC_2O_4 exactly as in the regular analysis. Continue the stirring two or three minutes after the addition of the hot $(NH_4)_2C_2O_4$ solution and then let settle till nearly clear which should occur in not over five minutes if the work is correctly done.

Decant through a 9 cm. filter, pouring off very close. The precipitate should be so dense as to render this easy. Add 30 c.c. of hot water to the precipitate, stir well and let stand three or four minutes and again decant. Repeat the decantation a third time and then transfer the precipitate to the filter and wash well three or four times using about 10 c.c. of hot water each time, allowing the precipitate to drain thoroughly after each washing.

Reserve the filtrate and washings for the determination of Magnesia.

Now run 10 c.c. of water through as before but catch it in a small separate beaker, add a little H_2SO_4 and one drop of the permanganate solution and warm. If the color is not discharged the precipitate is sufficiently washed; otherwise continue the washing and test again. Then wash the CaC_2O_4 back into the beaker in which it was precipitated, add water, if necessary, to make a volume of at least 150 c.c., place the beaker under the funnel and run through the filter into the beaker 30 c.c. of dilute H_2SO_4 (1 volume acid to 3 volumes water). Stir the contents of the beaker thoroughly while the acid runs in to avoid the separation of $CaSO_4$. Now wash the funnel and filter thoroughly with hot water. Dilute the liquid in the beaker to about 350 c.c. warm to 60° or 70° C. and titrate with the permanganate to a faint pink color not disappearing for two or three minutes.

To test the filter paper for undissolved CaC_2O_4 it may be added to the contents of the beaker and stirred up in it but if the washing has been careful it will not cause a discharge of the color.

The number of cubic centimetres of the permanganate used will equal the percentage of $CaCO_3$ in the sample, for if 1 c.c. equals .008929 gram, 100 c.c. would equal .8929 gram, the amount taken, or 100 per cent. if pure $CaCO_3$ was used.

THE DETERMINATION OF THE MAGNESIUM.

The filtrate and washings from the calcium precipitate should not exceed 350 c.c. When almost cool, add NH_4OH till distinctly alkaline then gradually a sufficient amount (10 to 20 c.c.) of Na_2HPO_4 solution, stirring vigorously during the addition; now slowly add $\frac{1}{10}$ the volume of strong NH_4OH and stir for four or five minutes. Let settle for one hour and filter through a 7 or 9 cm. filter. Wash the precipitate once or twice with ammonia water, then wash the beaker and precipitate thoroughly with 50 per cent. alcohol, allowing the precipitate to drain well each time. Continue the washing till the last filtrate diluted with water does not give an alkaline reaction with cochineal indicator. Place the precipitate and filter in the beaker in which the precipitation was made and stir up with about 100 c.c. of water, then add 2 c.c. of cochineal indicator and titrate with one-tenth normal H_2SO_4 to acid reaction; or add at once a measured excess of acid and titrate back with one-tenth normal ammonia.

1 c.c. of $\frac{1}{10}$ normal H_2SO_4 equals .0042 gram of $MgCO_3$. From this value, the number of c.c. of the acid required and the weight taken, calculate the percentage of $MgCO_3$.

PROCESS FOR CALCIUM WHERE MAGNESIUM IS PRESENT IN CONSIDERABLE AMOUNT.

Weigh out .8929 gram of sample, ignite and proceed as with low magnesia, but use more water in decanting and washing. After decanting two or three times, dissolve the calcium precipitate in a very little HCl, dilute to 200 c.c., add a few drops of $(NH_4)_2C_2O_4$ solution, heat and reprecipitate with NH_4OH. Let settle five minutes, decant and wash thoroughly. This re-solution need not

take much time if the precipitation is made in a very hot liquid and vigorously stirred. When the precipitate is thoroughly washed, transfer it to the beaker in which precipitation was made, dissolve it in H_2SO_4 and titrate with $KMnO_4$ as in the first process.

THE DETERMINATION OF THE MAGNESIUM WITHOUT SEPARATION OF THE CALCIUM.

This rapid method only applies to dolomites containing very little iron.

Weigh out .42 gram of sample into a beaker, add 20 c.c. of water 10 c.c. of concentrated HCl and then 3 or 4 drops of HNO_3, boil till solution is complete. Dilute to 150 c.c. add NH_4OH till just alkaline, heat to boiling and precipitate the calcium as usual, using 20 c.c. of a saturated solution of $(NH_4)_2C_2O_4$ diluted with its own volume of water and also heated to boiling. Stir vigorously for four or five minutes. Let the calcium precipitate settle for ten minutes. Cool the solution, and add NH_4OH till distinctly alkaline; then add gradually a sufficient amount of Na_2HPO_4 and stir well. Then add slowly $\frac{1}{10}$ the volume of strong NH_4OH and stir vigorously for four or five minutes. Let the mixed precipitates settle one hour, filter, wash with 50 per cent. alcohol and titrate with H_2SO_4 as before. CO_2 must be avoided in reagents and water as any $CaCO_3$ will titrate as magnesium.

NOTES ON THE VOLUMETRIC METHODS.

Ignition of the sample is necessary to destroy any organic matter present, which, if not destroyed, will reduce $KMnO_4$ and cause the calcium results to run high.

Unless the precipitate of CaC_2O_4 is stirred up in a considerable volume of water when the first few cubic centimeters of the H_2SO_4 are added to dissolve it, a dense flaky precipitate of $CaSO_4$ may separate, which is likely to occlude solution and obscure the end point.

If the $KMnO_4$ is added too rapidly during the titration, or the solution is not well stirred, brown MnO_2 may separate out; if this is not completely redissolved the results will be inaccurate.

All water used in diluting the solutions in this process for lime must be free from CO_2 or $CaCO_3$ will come down with the CaC_2O_4 and as this does not react with permanganate, the lime will come low. For the same reason it is important that all the CO_2 be expelled from the solution of the sample in HCl by boiling it thoroughly.

If the precipitation of the magnesium is made in an Erlenmeyer flask and the solution shaken well for five minutes, it can be filtered off in a few minutes.

In the magnesia titration the end reaction is more satisfactory if a considerable excess of acid is run in first, and when all the $MgNH_4PO_4$ is dissolved, the excess determined by titrating back with one-tenth normal ammonia. The number of cubic centimeters of ammonia used, deducted from the amount of acid taken, gives the acid needed for the $MgNH_4PO_4$.

In analysing dolomites or other high magnesian materials it is usually quicker to determine the magnesium in a separate sample as above described, than to consume time in concentrating filtrates. If more than a few tenths per cent. of iron are present the end reaction becomes very obscure from the action of the iron on the cochineal, rendering the process inapplicable unless the iron is first removed.

In the determination of magnesia, the precipitate after washing with ammonia water may be partially dried at ordinary temperatures till the ammonia is expelled and the washing by alcohol thus avoided. (Handy's process).

References on Volumetric Lime and Magnesia.

Fresenius. Quantitative Analysis.

Sutton. Volumetric Analysis.

Handy. Jour. Am. Chem. Soc. 1900. P. 31.

Meade. Jour Am. Chem. Soc. 1899. P. 746.

Ulke. Eng. Min, J. 1900. Vol. 69, p. 164,

Konnick. Jour. Soc. Chem. Ind. 1900. P. 564.

THE DETERMINATION OF IRON IN ORES.

Most iron ores give up practically all their iron to hydrochloric acid, provided the acid be strong and the ore sufficiently finely pulverized.

There is danger of loss of iron, probably mechanical, if a concentrated solution of $FeCl_3$ is boiled; hence, too great concentration of the solution and too hard boiling must be avoided.

If the residue from the action of HCl is white after ignition, the iron may be considered to be all extracted unless the ore contains TiO_2 in which case an insoluble compound of iron, phosphorus and titanium may remain, which will not color the residue. The presence of much titanium causes a milky appearance in the solution when diluted, and also causes the insoluble matter to run through the filter when washed.

In case of unknown ores it is safer to fuse the insoluble portion, as in a limestone, and determine the iron in this portion separately. (See the determination of silica in iron ores).

Sometimes previous ignition of the ore at a red heat will cause it to dissolve more completely.

Solution :—Pulverize the ore in an agate mortar; take a very little at a time and rub it until all trace of grit has disappeared when tested between the teeth or on the back of the hand.

Weigh out one gram, put it into a small dry beaker, brushing off the watch glass carefully. Add 25 to 30 c.c. concentrated HCl, cover the beaker with a watch glass and set it on a hot iron plate. Digest at a temperature just short of boiling until all the iron is dissolved, and on shaking the beaker the residue appears light and "flotant" and free from dark, heavy particles. This may take from fifteen minutes to one hour or more, according to the nature of the ore. Dilute the solution to two or three times its orignal volume and filter through a 5 cm. filter into a 100 c.c. measuring flask. Wash the residue on the filter till it is free from acid.

By taking care to let the wash water run through completely each time, and not more than half filling the filter, this can be accomplished with not to exceed 80 c.c. of filtrate. Dilute to the mark and divide into two equal portions, then determine the iron in each. The results should agree almost exactly, and their sum is the iron in one gram of the ore. Dry and ignite the insoluble portion. If it is not white, or if suspected of containing iron, fuse as in case of the insoluble residue in a limestone. The iron in the HCl solution is then determined and added to the main quantity.

A convenient way to divide the solution in the 100 c.c. flask without using a dried measuring flask, is to rinse out a wet 50 c.c. flask with a little of the solution, pouring this out into a beaker, and then filling the 50 c.c. flask to the mark. Add the remainder of the 100 c.c. to that used in rinsing, washing out the 100 c.c. flask with a little water. Half of the solution will now be in the 50 c.c. flask and half in the beaker with the water.

Where an ore is decomposed with difficulty by HCl the addition of 2 or 3 c.c. of $SnCl_2$ solution to the ore and acid in the beaker will greatly accelerate the action by causing reduction of the ore as it dissolves. In this case after the color and the nature of the residue shows complete extraction, carefully add a solution of $KMnO_4$ to the contents of the beaker until the yellow color of ferric chloride again appears, then dilute and proceed as usual. The object of the permanganate is to oxidize the large excess of $SnCl_2$. It can be omitted if care is taken to avoid such excess, but its use is generally safer. Instead of taking one gram of the ore and dividing the solution as described and duplicating the determination, a single portion of one-half gram may be dissolved, and if experience has shown the residue to be free from iron, the solution can be diluted, reduced and the iron determined without filtering, thus greatly shortening the time required; but it is not safe to let the residue of an unknown ore pass without examination.

THE VOLUMETRIC DETERMINATION OF IRON BY POTASSIUM BICHROMATE AFTER REDUCTION OF THE FERRIC CHLORIDE BY STANNOUS CHLORIDE.

The process depends on the following reactions.

1. A strongly acid solution of $FeCl_3$, if boiling hot, is almost instantly reduced to $FeCl_2$ by a solution of $SnCl_2$, the end of the

reaction being shown by the disappearance of the yellow color of the solution.

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$
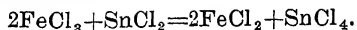
2. Any slight excess of tin solution can be removed by adding $HgCl_2$, which is reduced to $HgCl$, forming an inert, white precipitate without action on iron salts or bichromate, the $SnCl_2$ being converted into $SnCl_4$.

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl.$$
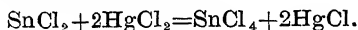
The reaction is not instantaneous and after the addition of the $HgCl_2$ at least two or three minutes should elapse before titration.

This reaction is satisfactory, *provided* too much $SnCl_2$ is not present and the $HgCl_2$ *is in large excess and added all at once*, otherwise metallic mercury may be formed as a gray precipitate, which will act on the bichromate solution and cause false results.

$$SnCl_2 + HgCl_2 = SnCl_4 + Hg.$$
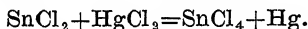
This reaction is at once detected by the *gray color* of the precipitate and entirely vitiates the results.

If the solution is very hot the difficulty of avoiding the reduction to mercury is increased.

3. When a solution of $K_2Cr_2O_7$ (potassium bichromate) is added to a solution of $FeCl_2$ containing a considerable excess of HCl the $FeCl_2$ is immediately oxidized to $FeCl_3$ with a corresponding reduction of bichromate.

$$K_2Cr_2O_7 + 14HCl + 6FeCl_2 = 2KCl + 2CrCl_3 + 6FeCl_3 + 7H_2O.$$

In the absence of an excess of HCl a basic chromium salt may separate as a precipitate and vitiate the results.

4. Solutions containing $FeCl_2$ strike an intense *blue color* with $K_3Fe(CN)_6$ (potassium ferricyanide), while solutions containing $FeCl_3$ give a yellow brown color. The ferricyanide solution must be fresh as it is reduced on exposure to light or on standing, and it must be *dilute* or its own color will interfere. The salt must be pure; some ferricyanide is contaminated with ferrocyanide and is worthless for this purpose.

PREPARATION OF THE SOLUTIONS.

1. *Potassium Bichromate Solution.* Fuse a sufficient quantity of the chemically pure salt in a platinum crucible. Apply the heat carefully and avoid all contact of the flame with the contents of the crucible as this will cause

reduction. As soon as the material fuses to a dark liquid, withdraw the lamp and let the crucible cool. During cooling the bichromate, after solidifying, will gradually crumble to powder.

Weigh out exactly 8.765 grams of this powder; dissolve it in 200-300 c.c. of cold water, transfer to a litre flask and dilute to 1 litre. 1 c.c. of this solution should correspond to exactly 0.01 gram of iron.

To test the solution, dissolve 1.4 grm. of *pure* ammonium ferrous sulphate, $(NH_4)_2Fe(SO_4)_2, 6H_2O$, in 50 c.c. of water containing 5 c.c. of HCl, run in from a burette 19 c.c. of the bichromate solution, stir well, then add a drop of the solution to a drop of the ferricyanide solution placed on a white porcelain plate. A blue color forms if ferrous iron is present. Now add the bichromate solution drop by drop, testing the liquid after each addition until instead of a blue, an orange yellow color is produced. The liquid in the burette should now read 20 c.c. If it does not, repeat the test and make a factor of correction. For example: if instead of 20 c.c. of bichromate, 20.2 c.c. were required, then $20.2 : 20 =$ any volume : the corrected volume; or $\frac{20}{20.2}$ is the factor by which any volume must be multiplied to give the equivalent volume of correct solution.

The object of the fusion of the bichromate is to expel water and destroy any trace of organic matter present.

If the salt is strictly pure and the fusion has been carefully conducted it will dissolve to a perfectly clear liquid which will check exactly on the iron salt if this is also pure. This makes a double check on the solution, and in important work chemicals should be obtained which will give it.

Much of the c. p. bichromate on the market contains excess of chromic acid and gives too strong a solution. This is possibly due to the presence of potassium tri-chromate or to sodium bi-chromate. For this reason the salt should always be purified by recrystallization. If too high a temperature is reached in the fusion, especially if the salt is not pure, the solution will be turbid. If more than a trace of this turbidity is present a new solution should be prepared.

2. *Stannous Chloride Solution.* Dissolve commercial "protochloride of tin" ("muriate of tin") in four times its weight of a mixture of three parts of water and one of HCl. Add scraps of metallic tin, and boil till the solution is clear and colorless. Keep the solution in a closed dropping bottle containing metallic tin.

3. *A Saturated Solution of Mercuric Chloride.* Keep an excess of the salt in a bottle and fill it up with water from time to time.

4. *A Very Dilute Solution of Potassium Ferricyanide.* Dissolve a piece half as big as a small pea in 40 or 50 c.c. of water. This solution must be made fresh when wanted as it does not keep.

The other solutions keep indefinitely. The $SnCl_2$ solution, however, absorbs oxygen and hence must be kept from the air; should it grow turbid or deposit a white precipitate, add more HCl and metallic tin and heat till clear.

PROCESS FOR THE ASSAY.

Transfer one-half the iron solution to a porcelain dish, add 5 c.c. HCl, heat to boiling, and drop in the tin solution slowly till the last drop makes the solution colorless. Remove the lamp and add a little cold water to cool the liquid. Then add at once 15 c.c. of the mercuric chloride solution, stirring the liquid with a glass rod. Let it stand three or four minutes. A slight white precipitate should form; if none, or a heavy *grayish* precipitate forms, the result is rendered doubtful or incorrect.

Now run in the bichromate solution until a drop of the liquid tested on the porcelain plate with a drop of ferricyanide solution no longer shows a blue, but a yellow color.

The number of cubic centimeters used, multiplied by two, gives the percentage of iron in the sample.

Repeat the process on the second half of the iron solution running in at once nearly the full amount of bichromate and then finishing drop by drop. If the two results nearly agree, average them. If by accident too much of the bichromate solution has been run in, add 1 c.c. of a dilute solution of $FeSO_4$, finish and read. Then add 1 c.c. more of the same solution; again finish and read. Deduct the difference between the first and second readings from the first reading to find the true end point.

In the case of mill cinder and other decomposable slags, add 20 c.c. of *water* to the finely powdered material, and stir up well to prevent the cinder caking on the bottom of the beaker; then add 20-30 c.c. HCl and proceed as before.

In the case of materials not attacked by HCl, fusion with Na_2CO_3 is necessary to get the iron into a soluble form.

Titanium will not affect this process, provided care be taken to fuse the residue and add its solution to the main filtrate. When zinc is used to reduce the solution TiO_2 will vitiate the results.

The presence of vanadium is said to vitiate the result, as it is reduced by the $SnCl_2$ and reoxidized by the bichromate.

THE DETERMINATION OF IRON BY TITRATION WITH PERMAN-GANATE OF POTASSIUM AFTER REDUCTION BY ZINC.

This is a widely used process. The time of the actual titration is shorter than with the bichromate, as no outside indicator is necessary, the end reaction being the permanent pink tint given to the liquid by the slight excess of permanganate.

On the other hand the permanganate solution is much more liable to change than the bichromate and is also much more subject to reduction by other materials, as for example, organic matter in the ore or solution.

Titration by permanganate in HCl solution is only permissible if a certain amount of manganous salt is first added to the solution, as otherwise the HCl will cause some reduction of the $KMnO_4$ giving a yellow-brown color and obscuring the end reaction.

The addition of phosphoric acid is desirable as it changes the yellow ferric chloride to ferric phosphate, which is colorless in HCl solution and does not obscure the end reaction.

Reduction of the solution by zinc is accomplished either by adding granulated zinc to the liquid in an Erlenmeyer flask and boiling a few minutes, as in the Emmerton phosphorus process; or still more expeditiously by using the "reductor" introduced by Mr. Clemens Jones, in which the iron solution is filtered through a column of granulated zinc.

Zinc is such a powerful reducing agent that many substances are reduced by it to oxidizable forms which tend to vitiate the results in iron. Thus the iron solution must not contain arsenic, titanium, vanadium or nitrates, since lower oxides will be formed which will reduce permanganate. Nitrates are reduced ultimately to ammonia which does no harm but frequently the reduction is only partial, forming hydroxylamine which acts powerfully on permanganate.

As the zinc is never perfectly pure, a "blank" must always be run upon it and the amount of this blank deducted from the permanganate used in the regular titration.

SOLUTIONS REQUIRED.

1. *Permanganate Solution.* A convenient solution is one in which 1 c.c. equals 0.01 gram of iron. This will contain 5.648 grams of $KMnO_4$ to the litre. The reaction is as follows:

$$KMnO_4 + 5FeCl_2 + 8HCl = KCl + MnCl_2 + 5FeCl_3 + 4 H_2O.$$

To prepare such a solution, dissolve 5.7 grams of pure crystallized $KMnO_4$ in water and dilute to 1 litre.

The solution should be prepared some time before standardizing. It is likely to alter rapidly at first, but in time reaches a comparatively stable condition if protected from light and dust.

Where large quantities are used, it is a good plan to make up a carboy ahead and let it be "aging."

To standardize this solution, use pure iron wire which can now be obtained for this special purpose. It contains 99.8 per cent. of iron.

Clean the wire by rubbing it with emery cloth and then with filter paper. Form it into a spiral by wrapping it around a small glass rod and cut into lengths corresponding to about 0.25 gram. Throw away the part held by the fingers while wrapping the spiral. Accurately weigh one of these pieces and put it in a small Erlenmeyer flask of about 75 c.c. capacity. This flask should be closed with a small glass bulb having a stem reaching down into the neck. This stopper prevents air from entering and causing oxidation of the solution. Add 20 c.c. of dilute H_2SO_4 (1:4), to the wire and then set the flask on a hot plate until the iron dissolves, avoiding violent boiling. When the iron is dissolved pour cold water over the bulb into the flask, thus washing down both the bulb and the neck of the flask. Transfer the liquid rapidly to a beaker, dilute to 200 c.c. and titrate without delay. The weight of the iron taken, multiplied by 0.998 and divided by the number of c.c. of the permanganate solution required will be the amount of iron equivalent to 1 c.c. of the solution.

The solution may then be diluted so as to make 1 c.c. equal to 0.01 iron, using water which has been boiled and while boiling treated with permanganate until it retains a very faint permanent pink color. It is more usual, however, to use the above value as a "correction factor" and to multiply the volume of permanganate used in the analysis by this factor.

In all work involving the use of potassium permangante use only Gay-Lussac or glass stoppered burettes as it is reduced by contact with rubber tubes.

2. *Titrating Solution.* This is made by dissolving 160 grams of manganous sulphate in water, diluting to 1750 c.c., adding 330 c.c. of phosphoric acid and 320 c.c. of sulphuric acid. Use the concentrated "syrupy phosphoric acid" of 1.725 sp. gr.

A simple form of this apparatus is shown in Fig. 2.
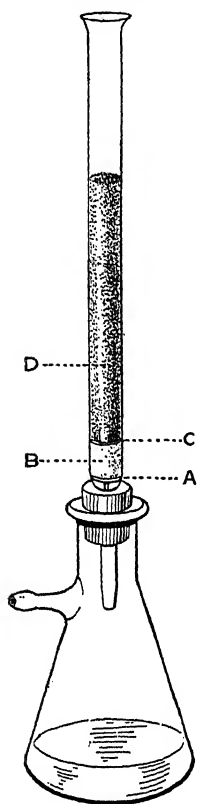
FIG. 2.
"REDUCTOR."

The large tube is about five-eighths inch inside diameter and is contracted at the bottom, and expanded into a funnel at the top. The stem enters the rubber stopper of the bottle, which is connected with a suction pump. The apparatus is filled as follows: A disc of stiff platinum foil A is cut a little smaller than the tube and rests on the contraction at the bottom; it is punched full of holes with a needle. A thin glass rod is fused into a hole in the center and this serves to hold it in place. Above the disc is about three-fourths of an inch of clean white sand B, which has been boiled with HCl and then washed to remove iron. Above the sand is a second perforated disc of platinum C. Above this the tube is filled with granulated zinc D for ten inches. This zinc must be of such a size that it will pass through a 20-mesh sieve, but not through a 30. It should be amalgamated before use, as follows: Moisten a quantity of it with very dilute sulphuric acid (about 3 c.c. to 100 c.c. of water), add a small drop of mercury and stir it in until the zinc shows uniformly the white mercury color. Wash the zinc free from acid and put it in the tube. Avoid more than just enough mercury. One-half gram is sufficient for 150 grams of zinc.

The solution to be reduced is poured into the funnel shaped top of the reductor. The rate at which it is drawn through must not be too rapid. Test this point by drawing an iron solution through and then adding some ammonium sulphocyanate to the re-

duced solution. If this gives a pink color the speed was too great and must be reduced by diminishing the suction. If air is drawn through the zinc in the reductor and immediately followed by dilute acid, the liquid running through is sometimes found to be oxidising, possibly from the formation of H_2O_2; hence, while running through the solution and wash water, the surface of the zinc must be kept continually covered with liquid.

If the reductor has stood unused for some time it should be washed out with dilute sulphuric acid and water before putting the solution through it.

PROCESS.

Weigh out 0.5 gram of the finely ground sample and ignite it in a porcelain crucible to destroy organic matter. Transfer it to a small beaker, add 10 c.c. of concentrated HCl, cover and digest till all the iron is in solution. Add 20 c.c. of dilute H_2SO_4 (1:1) and boil gently to expel some of the excess of HCl, then dilute to about 100 c.c. and filter, washing the the residue thoroughly. Dilute the filtrate to 200 c.c., using cold water, as the solution should be cool.

Now pour the solution into the zinc reductor and apply such suction that the liquid will flow through in a moderate stream. Follow the solution with 100 c.c. of 5 per cent. H_2SO_4, then with 150 c.c. of water, keeping the zinc covered with liquid during the entire process so that air will not be drawn through the zinc. As soon as the last wash water has passed through, disconnect the suction tube, pour the solution into a large beaker and rinse the flask out with a little water. Add 10 c.c. of the "titrating solution" and titrate quickly with $KMnO_4$.

The number of c.c. of $KMnO_4 \times$ factor $\times 2 =$ the percentage of iron.

Ignition of the sample is necessary unless organic matter is known to be absent.

The gentle boiling, after adding the dilute H_2SO_4, gets rid of most of the HCl. It is not necessary to expel all of it.

Determine the correction for the impurity in the zinc by running a blank with the same amount of water and acids used in the analysis, and deduct the volume of permanganate required in this from that used in the analysis.

The process should be checked on ores of known composition.

THE PERMANGANATE METHOD WITH REDUCTION BY $SnCl_2$.

This method is reliable, provided organic matter and sulphides are carefully destroyed by ignition of the ore and also that only a very slight excess of $SnCl_2$ is used. The precipitate of HgCl is slightly acted upon by $KMnO_4$ in strongly acid solutions; hence, titration must be made in very dilute cool solutions.

PROCESS.

Take 0.5 gram of ore, add a slight excess of $SnCl_2$ solution and 10 to 15 c.c. of HCl (1:1). Boil gently until the iron is all dissolved. This point is easily seen, owing to the light color of the solution, the $SnCl_2$ reducing the iron to the ferrous form. Now, if necessary, drop in more tin solution to complete the reduction. Then add 5 c.c. of a saturated solution of $HgCl_2$ to remove the excess of $SnCl_2$. Dilute the solution to about 250 c.c., add 5 or 10 c.c. of the "titrating solution," and then the standard permanganate solution until the last drop gives a persistent pink color. If excess of $SnCl_2$ has been added during the solution, oxidize it with permanganate and reduce again as described on page 29.

References on Iron:
Eng. Min. Jour., Vol. LVII, P. 342. Mixer and Dubois. Permanganate and Tin.
Jour. Am. Chem. Soc. 1893. P. 520. Dudley. Description reductor.
Jour. Am. Chem. Soc. 1899. P. 723. Shimer. Description reductor.
"Methods of Iron Analysis." P. 113. McKenna. Amalgamation of Zinc.

THE DETERMINATION OF SILICIOUS MATTER AND SILICA IN IRON ORES.

The portion of an iron ore insoluble in HCl, consists of free silica, various silicates, principally silicate of alumina, and not infrequently barium sulphate and titanic acid. Pyrite (FeS_2) is but slightly attacked by HCl and may remain in the residue unless some HNO_3 is added to the HCl. Spinel may be present occasionally in ores. Certain silicates, such as garnet, become soluble only after ignition; hence, when these are present, a preliminary roasting will increase the solubility of an iron ore.

The HCl solution of the ore is liable to contain silicic acid which must be separated by evaporation to dryness.

Treat one gram of the finely pulverized ore in a casserole or 4-in. porcelain dish with 25 c.c. concentrated HCl and a little HNO_3; evaporate the solution to dryness and heat on an iron plate until the residue is dry and scaly. Dissolve by warming in 10 c.c. concentrated HCl, dilute, filter onto a small filter, wash, ignite and weigh the "silicious matter."

Mix the ignited "insoluble silicious matter" with 6–8 times its weight of dry Na_2CO_3; fuse in a platinum crucible and extract with water. Acidify with HCl, evaporate to dryness and heat at a temperature not exceeding 120°C., until all odor of HCl has gone.

Add HCl and water, filter and wash with hot water, dry, ignite and weigh the SiO_2.

This filtrate may be evaporated to dryness and will usually be found to contain a small trace of SiO_2 not separated in the first evaporation. As noted before, the evaporation of the filtrate is a more efficient means of recovering all the SiO_2 than repeated evaporations before filtering. The second evaporation is not necessary unless very exact results are required, and in this case it is necessary to determine the impurity in the SiO_2 as follows.

To the weighed SiO_2 in the platinum crucible, add 1–10 drops concentrated H_2SO_4 (enough to moisten it); then add pure concentrated HFl until the SiO_2 is completely dissolved. Evaporate to dryness under a good hood, and ignite the residue. Deduct the weight of this from the weight of SiO_2 first found and the difference is pure SiO_2.

On treatment with hydrofluoric acid the silica is completely volatilized as gaseous silicon fluoride, while alumina, iron oxide, titanic oxide and barium sulphate remain unaltered.

Should the silica contain alkaline chlorides due to imperfect washing, these will be converted into sulphates, and the residue will be too heavy. This error need only be feared if there is considerable silica.

In case the ore contains spinel, this will neither be decomposed by the acid nor by the fusion, but will be found in the HFl residue and may retain some iron. It can be decomposed by prolonged treatment with dilute H_2SO_4 one volume of acid to one volume of water.

The combined filtrates in the above process can be used for an exact determination of the iron.

THE DETERMINATION OF PHOSPHORUS IN IRON ORES, IRON AND STEEL.

The methods in general use all depend upon first getting the phosphorus into solution as orthophosphoric acid, and then separating it from the iron and other bases in the form of ammonium phosphododecamolybdate, the so called "yellow precipitate."

The phosphorus in this is then determined directly or indirectly, and either gravimetrically or volumetrically.

This substance, when dried at 130 C, has uniformly the composition 12 MoO_3, $PO_4(NH_4)_3$. This formula requires 1.65 per cent. of phosphorus. The average of many most carefully conducted experiments has shown that the precipitate, if free from admixed molybdic acid or other impurities, contains 1.63 per cent. phosphorus within very narrow limits.

The precipitate is only obtained pure when formed under very exact conditions, and is easily affected by subsequent treatment, so that all methods depending upon the weighing of the "yellow precipitate" or its volumetric determination must be carried out rigorously according to the prescribed directions in every detail.

When a solution of ammonium molybdate in nitric acid is added to an acid solution containing phosphoric acid, the whole of the phosphoric acid is precipitated as the yellow "ammonium phosphomolybdate," under the following conditions.

1. All the phosphorus must be present as tribasic (ortho) phosphoric acid.

2. A decided excess of ammonium nitrate or sulphate should be present.

The precipitation is most rapid when the solution contains between five and ten per cent. of the salt.

3. A certain excess of free acid must be present — preferably nitric or sulphuric. This must amount to at least 25 molecules of acid for each molecule of P_2O_5 present, and must be increased when sulphates are present.

4. Too great an excess of free acid must be avoided, as this causes decomposition and partial re-solution of the precipitate.

This action becomes perceptible when over 80 molecules of acid are present to each molecule of P_2O_5. The concentration of the acid is also important; the smaller the volume of liquid the less free acid must be present.

This solvent action of free acid is prevented by a sufficient excess of molybdic acid solution, which excess must be greater as the amount of free acid is greater. It is also largely overcome by a considerable excess of ammonium nitrate.

5. The yellow precipitate is insoluble in the solution of molybdate of ammonia in nitric acid; also in solutions of ammonium salts, if neutral or only very *slightly* acid, but if *strongly* acid they attack the precipitate, which is, however, reprecipitated by the addition of molybdic acid solution to the liquid. It is also practically insoluble in a solution of potassium nitrate when neutral and not too dilute. Solutions of salts of organic acids usually dissolve the precipitate to some extent. From these solutions nitric acid and ammonium nitrate, in some cases, reprecipitate the compound; in others, e. g., with tartaric acid, or oxalic acid, probably not completely.

The mineral acids, HCl, HNO_3, H_2SO_4, all have a solvent action on the precipitate even in the presence of ammonium nitrate. HNO_3 has the least, HCl probably the most.

Pure water has a tendency to decompose the precipitate to a slight extent and make it run through the filter.

6. Precipitation is much more rapid from hot than from cold solutions, but in time it is probably complete at any temperature The precipitate from hot solutions is denser and more crystalline; from cold, finer and more granular, and harder to filter and wash.

7. Agitation greatly accelerates precipitation in this as well as in other chemical reactions.

8. The precipitate dried to constant weight at ordinary temperatures retains a little acid and water, which it loses when dried at 130° C. By washing the precipitate with a neutral solution of ammonium or potassium nitrate or by prolonged washing with water, it can be freed from acid without drying.

9. SiO_2 in the solution does not seem to interfere with the complete precipitation of phosphorus as yellow precipitate, but a small trace of the SiO_2 usually comes down with the precipitate, especially if the solution is too concentrated, or too warm, or stands too long. If the solution is rather dilute, not too hot, and is filtered promptly, the yellow precipitate can be obtained in the presence of considerable SiO_2 and practically free from it. Titanic acid does not prevent though it greatly delays the precipitation of phosphorus by molybdic acid solution.

10. Organic matter has usually been supposed to interfere with the precipitation of phosphorus, but it is probable that in many cases, noticeably in steel analysis, the bad results attributed to this cause were due to the fact that the phosphorus had not all been converted into the tribasic acid. The pyro- and meta-phosphoric acids are not completely precipitated by molybdic acid solution.

11. When arsenic acid is present in the solution with the phosphorus, some of it will be precipitated at the same time, the amount increasing with the temperature. Only very small traces come down at temperatures not exceeding $25°$ C.

12. MoO_3 may separate with the yellow precipitate as a light crystalline deposit. This free MoO_3 is soluble in acids with difficulty and cannot be washed out of the yellow precipitate. Its separation must always be guarded against when the yellow precipitate is to be weighed or titrated. It forms when the solution contains too much MoO_3, is too concentrated, or too dilute, too strongly acid or too nearly neutral. Too high a temperature precipitates it. The addition of strong HNO_3 to a solution of molybdic acid will sometimes precipitate it, as will the adding of molybdic acid solution to solutions of iron in concentrated nitric acid. Long standing favors the separation of excess of MoO_3 with the yellow precipitate. A finely divided form of the precipitated MoO_3, sometimes occurs, easily mistaken for "yellow precipitate" and liable to escape notice.

13. When the yellow precipitate is thrown down in a solution containing much iron and not sufficient acid, basic iron salts are likely to accompany it, making it reddish in color. This is especially the case when the solutions are hot.

14. The yellow precipitate, if pure, is easily and completely soluble in NH_4OH, (if it contains iron the solution will be turbid from the formation of ferric phosphate). From this solution the phosphoric acid is completely precipitated by "magnesia mixture" as $MgNH_4PO_4$. If the yellow precipitate contains any SiO_2 this will also, in part at least, dissolve in the NH_4OH and separate with the magnesia precipitate, making it a little flocculent. By cautiously adding HCl to the NH_4OH solution of the yellow precipitate until nearly neutral, and letting it stand for some time in a warm place, the SiO_2 separates completely and may be filtered off. The phosphorus may then be precipitated in the filtrate. In precipitating phosphoric acid with magnesia mixture, add the reagent drop by drop and stir the liquid constantly, so that the precipitate separates slowly and in a crystalline form, otherwise it will be impure, containing magnesia in excess and molybdic acid. The $Mg_2P_2O_7$ must be ignited thoroughly and with access of air to drive off any trace of MoO_3 it may contain.

For properties of the "yellow precipitate" and the effects of impurities and associated substances, see

Hundeshagen, Zeits. An. Chem., vol. XXVIII, p. 141; also Chem. News, vol. LX, p. 169.

Drown—Trans. Inst. Min. Engrs., vol. XVIII, p. 90.

Shimer—Trans. Inst. Min. Engrs., vol. XVII, p. 100.

Hamilton—Jour. Soc. Chem. Ind., vol. X, p. 904.

Babbitt—Jour. An. and App. Chem., vol. VI, p. 381.

Pattinson—Jour. Soc. Chem. Ind., vol. XIV, p. 443

Mahon—Jour. Am. Chem. Soc. 1898, p. 429.

Baxter—Am. Chem. Jour. vol. 28, p. 298.

On the precipitation by magnesia—

Gooch—Am. Chem. Jour., vol. I, p. 391.

GRAVIMETRIC METHOD FOR PHOSPHORUS WITH FINAL PRECIPITATION AS MAGNESIUM AMMONIUM PHOSPHATE.

This method is free from the chances of error due to the presence of MoO_3 in the the yellow precipitate. It is gravimetric, and the phosphoric acid is finally weighed in a form not subject to variation in composition. It is applicable to all kinds of material and to any percentage of phosphoric acid; hence, it is a standard method to which final reference must be made in all important determinations.

Process for Iron Ores.—In the absence of more than traces of titanium or arsenic. Weigh 1 to 5 grams, according to the percentage of phosphorus, of the very finely pulverized ore. Put it into a 4-inch porcelain dish or casserole, add 1 c.c. HNO_3, then concentrated HCl, using 10 c.c. for each gram of ore taken, and then add 15 c.c. more (*i. e.* for three grams use 45 c.c.). Cover with a watch glass and warm till all the iron appears to be in solution, then boil down to dryness, keeping covered to avoid spattering. Dry on a hot plate till the acid is expelled, then add from 30 c.c. to 50 c.c. concentrated HCl, cover and digest till all the iron is dissolved. Now boil down until the volume of the liquid does not exceed 10 or 15 c.c. If the dish is kept covered there need be no formation of dry salt on the sides. Add water till the volume is 40 or 50 c.c., washing off the cover and the sides of the dish. Filter into a No. 1 or 2 beaker, using a small filter. Transfer the residue to the filter and wash until there is no acid taste to the washings.

Dry and ignite the *residue.* With ordinary ores, if light colored and not too large in amount it is practically free from phosphorus, and may be thrown away. In special or doubtful cases, however, fuse it, like the insoluble residue from a limestone, and after filtering out the silica, add ammonia to the filtrate, heat to boiling and let the precipitate of $Fe(OH)_3 + Fe(PO_4)$ settle. Decant off the clear liquid, dissolve the precipitate in a little HNO_3, add 20 c.c. of molybdic acid solution and warm. Should a "yellow precipitate" separate, it must be added to that obtained from the main solution.

In some cases treatment of the residue with acid after it has been ignited will extract the remainder of the phosphorus.

Such ores should be ignited after weighing out, and will then usually give a residue free from phosphorus.

Always test the residue from very low phosphorus ores.

The filtrate and washings from the insoluble matter of the ore should not exceed 150 c.c. To these add 10 c.c. of concentrated HNO_3, and then NH_4OH, until a precipitate is formed which does not disappear on stirring. Then add 3 c.c. of concentrated HNO_3, which must redissolve the precipitate and give a clear, amber colored liquid, not at all *red* in tint. The solution will now be quite warm. Add at once from a pipette in a fine stream 50 c.c. of "molybdic acid solution."* Stir the liquid vigorously while adding the reagent and for about three minutes afterwards. Let the solution stand in a warm place until it is clear and the precipitate has all settled (which should not require more

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* *Preparation of the Molybdic Acid Solution.*—Add to 100 grms. of molybdic acid, 300 c.c. of water, and then 120 c.c. of NH_4OH 0.90 sp. gr. This will dissolve the MoO_3. The solution must smell distinctly of ammonia, if it does not, add more NH_4OH. Unless the solution is clear, filter it, then dilute to about 800 c.c. Now mix 500 c.c. of conc. HNO_3 with enough water to make about 1200 c.c. Cool both solutions and mix by *pouring the solution of molybdic acid into the diluted HNO₃.* The volume should now be about 2000 c.c. Let mixture stand a day or two, or until any small precipitate settles and use the clear liquid. If the solution of molybdic acid in NH_4OH is not diluted sufficiently, or if the above directions are not followed as to mixing, the molybdic acid may separate from the solution. 40 c.c. of this solution will precipitate about 0.04 grms. of phosphorus. Pure MoO_3 must be used in this formula. Some of that on the market is principally ammonium molybdate containing water and ammonia. It should be tested by gently igniting a small quantity and determining the loss of weight. Calculate only the non-volatile portion as MoO_3 in preparing the solution.

than one hour), remove a portion of the clear liquid with a pipette and test it by adding a little more molybdic acid solution and warming, to make sure that all the P_2O_5 is down.

Filter the liquid through a 7 cm. filter. Transfer the precipitate to the filter and wash free from iron, with a 5 per cent. solution of ammonium nitrate *very slightly acidified* with HNO_3. The washing must be thorough or difficulty will be experienced when dissolving the precipitate, as phosphates of iron and alumina may form and clog up the filter. When the precipitate is washed, put the beaker in which the precipitation was made, under the funnel, and redissolve the precipitate on the filter with 20 to 30 c.c. of dilute NH_4OH (about one part of concentrated ammonia to four of water). When it is dissolved and the liquid has all run through, wash the filter three or four times with water, then with a little dilute HCl, to dissolve any ferric or other insoluble phosphate present, and finally with water. Use care in washing, letting each portion of water run through before adding another so as to keep the volume of the filtrate small. This should not exceed 100 c.c. and is usually much less. The filtrate should now be clear and colorless. If it is cloudy or colored (due to a little iron), add HCl until the liquid is acid (the yellow precipitate usually separates), then add four or five drops of a saturated solution of citric acid, then NH_4OH to make the liquid strongly alkaline. This will give a clear liquid, the citric acid holding the iron in solution.

Now add drop by drop a considerable excess of "magnesia mixture," * stirring the liquid constantly. Estimate the amount from the probable percentage of phosphorus

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* *Preparation of "Magnesia Mixture."*—Dissolve 22 grms. of dry calcined magnesia in as little HCl as possible. When dissolved add more of the magnesia until some remains undissolved, now boil; any iron oxide, alumina and phosphoric acid present will be precipitated. Filter the solution, add 280 grams NH_4Cl, 800 c.c. water and 200 c.c. conc. NH_4OH (sp. gr. 0.90). When all dissolves, dilute to 2000 c.c. Let stand a day or two and decant or filter the solution from any precipitate. 10 c.c. of this reagent will precipitate about 0.07 gram of phosphorus.

in the ore taken. Continue to stir the solution vigorously for four or five minutes, then add NH_4OH until the solution smells strongly of ammonia. Let it stand until the precipitate of $MgNH_4PO_4$ has settled completely (one or two hours). The precipitate should be *white and crystalline;* if red or flaky, the results will be inaccurate. Filter onto a small filter or better onto a Gooch perforated crucible. Wash with water containing $\frac{1}{10}$ its volume of concentrated NH_4OH and a little NH_4NO_3, dry, ignite and weigh as $Mg_2P_2O_7$. This contains 0.279 of phosphorus.

It is essential that the filtrate from the phosphorus precipitate should give at once a strong reaction for magnesium when tested with a drop of a solution of sodium phosphate, as a considerable excess of reagent is necessary to completely precipitate the phosphorus.

Modification of the Process for Ores Containing Titanium. When ores contain titanium in any amount, the residue will contain iron and phosphorus. The solution of the ore may become turbid on dilution, and the residue run through the filter on washing.

Some of the titanium usually goes into solution and may delay the precipitation of phosphorus. In such cases a larger excess of molybdic acid solution should be used, and a longer time given for the separation of the precipitate.

Weigh out the ore and dissolve it in HCl as in the regular process. If the filtrate from the insoluble residue is not clear add a little HNO_3 and warm, which will probably clear it. If a slight turbidity remains it is of no importance and may be neglected. Now proceed with the filtrate as in the regular process. After the yellow precipitate has been dissolved in ammonia and the filter washed as directed, dry and burn the filter and add the ash to the insoluble residue. This is necessary, as insoluble compounds of phosphorus and titanium may be retained in the filter. This residue is now mixed with eight times its weight of dry Na_2CO_3 and fused as for silica. Boil the fusion with water until thoroughly disintegrated. The phosphorus passes into solution as

phosphate, while the TiO_2 remains insoluble as titanate. Filter the liquid from the insoluble matter, acidulate the filtrate with HNO_3, and evaporate it to dryness. Add a little HNO_3, then water and filter from the separated SiO_2.

Add to the filtrate 25 c.c. molybdic acid solution and warm, filter off the yellow precipitate and treat it exactly like that from the main solution. Add the phosphorus thus obtained to that obtained from the first solution.

The foregoing treatment is satisfactory for ores with moderate amounts of TiO_2. Where much is present, direct fusion of the ore is advisable.

See a valuable paper by Drown and Shimer, Trans. Inst. Min. Engrs., vol. X, p. 137. Also, Pattinson. Jour. Soc. Chem. Ind. 1895, p. 443. Discussion, p. 1022.

When ores contain arsenic there is always danger that the final results will be high from the presence of magnesium arsenate.

In this case proceed as follows. To the filtrate from the insoluble residue, which should be in a small Erlenmeyer flask, add a solution of Na_2CO_3 until the liquid becomes dark colored, then add gradually a solution of pure crystallized sodium sulphite (Na_2SO_3) prepared by dissolving the salt in water 1 to 5, and adding HCl until the solution reacts slightly acid. Warm the iron solution up to boiling, shaking occasionally. If any precipitate forms, redissolve it with a few drops of HCl. By this time the solution should be *colorless* and all the iron reduced to the ferrous state; if not, continue the warming. When reduced add 10 c.c. HCl, and boil until the odor of SO_2 has gone (usually about three minutes). Remove from the flame and pass a stream of H_2S gas through the liquid for fifteen or twenty minutes, or till all the As_2S_3 is precipitated. (The volume of the liquid should not exceed 150 c.c.) The As and any Cu present separate completely as *sulphides*. Filter the solution rapidly into a beaker and wash with a little H_2S water. Now boil the filtrate till all the odor of H_2S has disappeared, then add HNO_3 drop by drop to the hot liquid until the change of color shows that the iron is changed to the ferric state. The liquid should become perfectly clear. A faint cloud of separated sulphur may form, but will disappear on heating and does no harm. From this point proceed exactly as with the filtrate from the insoluble residue in ores when As is not present.

The process depends upon the complete precipitation of arsenic by H_2S in hot strongly acid solutions. The reduction of the iron is necessary to prevent a large separation of sulphur from the action of the H_2S on the $FeCl_3$.

The As_2S_3 precipitate may be used for the determination of arsenic, provided the solution has not been boiled before precipitation by H_2S, which would cause volatilization of $AsCl_3$. See Fresenius Quantitative Analysis for details.

DETERMINATION OF PHOSPHORUS IN BLACK BAND AND OTHER ORES WHICH CONTAIN MUCH CARBONACEOUS MATTER.

These should be weighed out in a porcelain crucible and ignited, taking care not to heat so rapidly as to cause loss by blowing out of fine particles. Set the crucible on its side over a small flame and let the material gradually burn away until all carbon is gone, and an "ash" is left. Treat this by the regular process. Avoid a high temperature in burning or the material will *cake*, thus delaying the combustion, and leading to imperfect solution. A dull red heat is sufficient.

DETERMINATION OF PHOSPHORUS IN MILL CINDER.

Two points here need attention. *First*, the material being a soluble silicate, it should be decomposed by weak acid and evaporated to dryness, as in the determination of silica after fusion. *Second*, all mill cinder contains particles of metallic iron, in which phosphorus is present as phosphide. These would evolve PH_3 gas when dissolved in HCl, so HNO_3 must be used to oxidize this phosphorus. Proceed as follows. Weigh 1 gram into a porcelain dish, add 20 c.c. HNO_3 1.2 sp. gr., stir well to prevent caking and warm till action ceases, then add 10 c.c. H_2O and 10 c.c. concentrated HCl. Evaporate to dryness and heat on an iron plate to 200°C. for half an hour. Add 10 c.c. HCl, and digest till all the iron is dissolved. Dilute, filter, and proceed as with an ore.

DETERMINATION OF PHOSPHORUS IN IRON AND STEEL BY THE MOLYBDATE-MAGNESIA PROCESS.

The phosphorus in iron and steel exists principally as *phosphide*. When these metals are treated with ordinary oxidizing solvents, such as dilute HNO_3 or $KClO_3+HCl$, the oxidation of the phosphorus is incomplete; when treated with non-oxidizing acids (HCl or H_2SO_4), part of the phosphorus passes off as gaseous PH_3. Even concentrated HNO_3 fails to convert all the phosphorus into tribasic phosphoric acid.

These metals also contain carbon compounds which pass into solution in HNO_3, forming a dark colored substance, and the presence of this dissolved carbonaceous matter is generally supposed to interfere with the precipitation of the yellow precipitate. It seems probable, however, from certain experiments that, if the phosphoric acid is in the tribasic state, this organic matter is without influence. It is certain, however, that unless the oxidizing action is strong enough to destroy this carbonaceous matter completely, the phosphorus is not all oxidized and hence not precipitated completely.

The oldest and most certain method of oxidation is the "dry method." It consists in dissolving the metal in HNO_3 either concentrated or dilute, (sp. gr. 1.2) and then evaporating the solution to dryness. The dry mass of basic ferric nitrate is then heated to about 200° C. for some time. At this temperature the salts are decomposed, the iron largely converted to ferric oxide. and the dissolved carbon and the phosphorus completely oxidized. This residue can then be dissolved in HCl and treated like an ore. The method is always reliable and involves no delicate adjustments.

To save the time required for evaporating the solution and baking the residue, several methods have been devised for oxidizing the material in the nitric acid solution. The reagents most successfully used are potassium permanganate and chromic acid. Aqua regia, potassium chlorate or chlorine fail to oxidize the material completely.

When permanganate is used there is a separation of MnO_2 as a brown precipitate which holds phosphorus and must be entirely redissolved before filtering from the residue or precipitating the phosphorus. This is accomplished by adding a reducing agent, such as oxalic acid, ferrous sulphate, sugar, or potassium nitrite, to the acid liquid. Any considerable excess should be avoided. The MnO_2 is reduced to MnO and dissolved in the acid.

Wet methods are more rapid but are not adapted to all kinds of material and must only be used where they have been shown to apply by repeated checking of the results with the standard methods.

When pig iron or steel, containing silicon, is dissolved in HNO_3, evaporated and "baked," the HCl solution of the residue will be found to filter very slowly because silicic acid in HNO_3 solution is not fully dehydrated on evaporation even if the residue is heated to 200° C. Hence when the residue is treated with HCl some of the SiO_2 goes into the solution and leaves the rest in a highly gelatinous form.

The SiO_2 left after the evaporation of an HCl solution is much more granular and easily filtered off. Therefore, in all cases where silicon is present to any extent the HCl solution of the "baked" residue should be evaporated to hard dryness and again taken up in HCl. This second evaporation takes but little time and is essential, especially with cast iron, if a long and tedious filtration is to be avoided.

It is stated that the addition of a few drops of HFl or a little NH_4Fl to the first HCl solution will cause it to filter more rapidly and often render the second evaporation unnecessary.

Process for Phosphorus in Iron and Steel.—Take from 1 to 5 grams of the well mixed borings. Treat them in a covered casserole or dish with 25 to 75 c.c. of HNO_3 sp. gr. 1.2 (made by mixing water and concentrated HNO_3 in equal volumes). Add the acid cautiously to prevent boiling over. Heat till action has ceased and boil down to dryness, using care to prevent spattering, and keeping the dish covered. When dry, set on a hot iron plate and heat the dish to about 200°C. for from 30 minutes to 1 hour; at the end of this time the material should be hard and scaly and show no trace of acid fumes. Now add from 15 to 25 c.c. concentrated HCl, and digest till the iron is dissolved. Again evaporate to hard dryness and dissolve a second time in concentrated HCl, then proceed as with an iron ore.

Many *steels* will leave no residue insoluble in HCl. In this case filtration as well as the second evaporation is unnecessary.

The phosphorus retained in the residue, practically amounts to nothing in the case of irons and steels.

To make the filtration easy, add to the above HCl solution about 50 c.c. water and boil for about 5 minutes. Then let it settle completely, decant off the clear liquid through the filter, and transfer and wash the residue with warm water, adding a little HCl at first. This treatment seems to cause a consolidation of the SiO_2.

PROCESS FOR FERROSILICON AND OTHER DIFFICULTLY SOLUBLE ALLOYS.

Ferrosilicon with over 10% of Si is only slightly attacked by HNO_3 or aqua regia. This and other insoluble alloys cannot be

treated by the foregoing method for the determination of phosphorus. With ferrosilicon, if the percentage of Si is not too high, the addition of a little HFl or NaFl to the HNO_3 and metal in the dish will cause it to dissolve and then the regular method can be followed. About as much NaFl should be added as there is Si present. The metal should be very finely pulverized; this presents no difficulty as these alloys are all brittle. The metal should be crushed in a steel mortar until it will all go through a 100 mesh sieve and then the portion used in the analysis rubbed down in an agate mortar.

Samples not attacked by the fluoride must be fused. Mix the very finely ground sample with five or six times its weight of a fusion mixture of equal parts of $NaNO_3$ and Na_2CO_3 and fuse in a platinum crucible. Apply the heat cautiously until the first reaction is over and the mass is quiet, then raise the temperature till fusion is complete. Avoid using a higher temperature than is necessary as the platinum is likely to be attacked. The fusion can then be taken up in water and HCl and the phosphorus determined as usual.

HCl must not be added in the crucible or Cl may be formed and attack it, but after the mass has been soaked out with water any adhering Fe_2O_3 may be dissolved in a little HCl.

Instead of dissolving the whole fusion in HCl, it may be boiled with water, the lumps being crushed fine, and the solution then filtered from the Fe_2O_3 and acidified; the filtrate will contain all the phosphorus as sodium phosphate with some SiO_2. The residue should be tested however in important cases. A blank must be run on the reagents.

Sodium peroxide is sometimes used instead of the nitrate; it works rapidly and is a powerful oxidizing agent, but is not so easy to obtain pure. It acts at so low a temperature that nickel crucibles can be used in the fusions and the wear on the platinum saved. These fusions are very destructive to platinum, which should not be used when the metal is fused with Na_2O_2 alone.

In fusing ferrosilicon with sodium peroxide alone a large excess of the reagent must be used or the reaction becomes very violent; at least eight parts of peroxide to one of metal are required. The temperature of fusion need not exceed a dull red.

Blair.—Chemical Analysis of Iron, 4th Ed. p. 105.

DETERMINATION OF THE PHOSPHORUS BY WEIGHING THE YELLOW PRECIPITATE.

This method is very generally used as a "rapid method."
That the yellow precipitate obtained may be of uniform compo-

sition, the details of the process must be carried out exactly as given.

As the yellow precipitate contains 1.63% of phosphorus it is convenient to take for analysis that quantity of the material in grams. The weight of the precipitate in grams will then be the percentage of phosphorus.

The drying and weighing of over 0.4 gram. of yellow precipitate is difficult, hence for ores having over $\frac{4}{10}$% of phosphorus, take $\frac{1}{2}$ the above amount (0.815 gram.).

The following details are essentially those given by E. F. Wood in Zeits. Anal. Chem., vol 25, p. 489:

Process for Iron Ores.—Weigh 1.63 grams of the finely pulverized ore into a 4-inch dish or casserole, add 25 c.c. concentrated HCl, digest, evaporate to dryness, and heat as in the former process. Now add 20 c.c. HCl, and digest till all the iron is dissolved. Add 30 c.c. water, boil, let settle and filter into a beaker of about 200 c.c. capacity; wash with small portions of water, letting each run through before adding the next. The volume of filtrate and washings need not exceed 70 or 80 c.c. Now add 35 c.c. concentrated HNO_3, and boil down rapidly until the volume of the liquid is 15 c.c. (judged by putting this amount of water in a similar beaker and comparing the two). Take off of the hot plate, wash off the cover and add water. Altogether from 15 to 20 c.c. of water should be added; that is, at least as much water as there was liquid. Stir the solution and add from a pipette 40 c.c. of molybdic acid solution which should be at a temperature of not less than 25°C so that the mixed solution shall be at a temperature of not less than 40°C. Stir vigorously for 2 or 3 minutes, set in a warm place (*not* on a hot plate or water bath, which may cause precipitation of molybdic acid) until the precipitate has settled and the liquid is perfectly clear—this will take 30 minutes to an hour according to circumstances.

Fold a small filter of about 4 cm. diameter, put it in an air bath and dry it at 110° C. for 15 minutes. Then take it rapidly to the balance and weigh it to the nearest milligram.

Do not swing the balance but simply weigh to a stand still.

Place the paper in a small funnel, filter and transfer the precipitate to it. Considerable time may be saved if the clear liquid is first drawn off by a small siphon or with a pipette; this can be done with a little practice, so as to leave but a few c.c. of liquid above the precipitate. If care is taken not to disturb the precipitate only the remaining liquid need be filtered, and the filtering of 30 or 40 c.c. of liquid is avoided.

Wash the precipitate carefully six times at least, with water containing 1 per cent. of HNO_3, set the funnel and contents in an air bath and dry at 110° to 120°C for 30 minutes after all visible moisture has disappeared. Then rapidly take the filter to the balance and weigh as before. The difference between the second weight and the first gives the weight of the yellow precipitate, and this in grams gives the phosphorus in per cent.

Process for Iron and Steel. — Weigh 1.63 grams of the well mixed borings into a four inch covered dish or casserole. Add cautiously 35 c.c. HNO_3 sp. gr. 1.2, boil to dryness, then bake for thirty minutes on a hot iron plate at 200° C. Dissolve in 20 c.c. HCl and if silicon is present again evaporate to dryness and dissolve a second time. Now proceed as in the case of ores, except that if the steel dissolves without residue filtration is unnecessary.

The above methods assume that the phosphorus all passes into solution and that arsenic is absent. Titaniferous and arsenical ores and metals must be treated by the first method.

The yellow precipitate method, as described, may be much shortened for steel and some pig irons by using wet methods of oxidation. For the use of permanganate see Volumetric Method for Phosphorus on page 59.

The Chromic Acid Method as used at Homestead, Pa., and described by Mr. Unger, is essentially as follows.

Dissolve 1.63 grams of steel in 30 c.c. of nitric acid, sp. gr. 1.20 in a 175 c.c. Erlenmeyer flask. Place the flask over a burner and evaporate to 15 c.c. Add to the boiling solution 20 c.c. of a solution of 30 grams of CrO_3 in 2000 c.c. of HNO_3 sp. gr. 1.42. Dissolve the chromic acid by heating. This solution will only keep about two weeks.

Evaporate the contents of the flask to 18 c.c. wash down with 5–7 c.c. of water, cool to 40°–45° c.c. and add 30 c.c. of clear molybdic acid solution which should be previously heated to about 40°C. Cork the flask and shake 5 minutes as in the Emmerton process. Let settle fifteen minutes, filter, wash and weigh as in the original process.

When using this process silicon should be practically absent.

VOLUMETRIC METHODS FOR PHOSPHORUS.

These are based on the precipitation of the phosphorus as phosphomolybdate and determination of the amount of the precipitate by estimating the molybdic acid contained in it volumetrically, either by reduction with zinc and titration with potassium permanganate or by neutralizing it with standard alkali.

EMMERTON'S METHOD. TITRATION BY PERMANGANATE.

When the yellow precipitate is dissolved in NH_4OH and mixed with a very considerable excess of H_2SO_4 it all remains in solution. If this solution is warmed with metallic zinc, zinc dissolves, hydrogen is given off, and the molybdic acid is rapidly reduced, giving first a dark red and finally a green solution containing, if the reduction is complete, Mo_2O_3. If this solution is rapidly filtered from any undissolved zinc, it can be titrated with a solution of potassium permanganate which promptly oxidizes the Mo_2O_3 back to MoO_3. The solution becomes colorless and finally when oxidation is complete is colored pink by the least excess of permanganate.

The color of the reduced solution depends somewhat upon the excess of sulphuric acid present. If this is too large the green color will not be reached and the end of the reduction cannot be determined. The smaller the excess of H_2SO_4 the sharper is the change from red to green at the end.

Complete reduction is a matter of considerable difficulty and the methods in use do not always attain it. This has given rise

to the assigning of various formulæ to the reduced product. Emmerton gives $Mo_{12}O_{19}$, which probably most nearly represents the usual product of the reduction method he describes. The Reductor gives ratios between the Mo and the O which vary with the the method of using it. Blair and Whitfield give for the Reductor product $Mo_{24}O_{37}$.

Emmerton. Trans. Am. Inst. Min. Engs. vol. XV, p. 93.
Dudley and Pease. Jour. Am. Chem. Soc. 1894. p. 224.
W. A. Noyes. Jour. Am. Chem. Soc. 1894. p. 553.
W. A. Noyes. Jour. Am. Chem. Soc. 1895. p. 129.
Blair and Whitfield. Jour. Am. Chem. Soc. 1895. p. 747.
Auchy. Jour. Am. Chem. Soc. 1896. p. 955.

This uncertainty as to the reduction product makes the standard permanganate solution of uncertain value in phosphorus if standardized against metallic iron only; hence it is better to check it against a standard steel, ore or pig iron, of known phosphorus content which should be treated exactly by the method used in the regular analysis.

The widely extended use of this method shows, however, though there is some uncertainty as to the nature of the oxide produced by reduction, this possibly being different for different workers, that working always in exactly the same way, the reduction is uniform, and hence the titration is a reliable method for estimating the yellow precipitate, and indirectly the amount of phosphorus.

PROCESS.

1.—*Preparation of the Solution of Potassium Permanganate.* To compute the strength of this solution assume that the reduction of the "yellow precipitate" gives $Mo_{12}O_{19}$. Then the permanganate solution must furnish 17 atoms of oxygen for each 12 of MoO_3 present before reduction. The yellow precipitate contains 24 MoO_3 to 1 of P_2O_5 or 12 of MoO_3 to 1 of P; hence the permanganate must furnish 17 atoms of oxygen for every atom of phosphorus present in the precipitate.

To standardize the permanganate solution on iron.

Two atoms of iron, as FeO, require one atom of oxygen to produce Fe_2O_3; hence, 34 atoms ($= 2 \times 17$) of iron as ferrous salt will consume as much oxygen from permanga-

nate as will the reduced molybdic acid, equivalent to one atom of P in the yellow precipitate.

One atom of phosphorus $= 31$, and 34 atoms of iron $= 1904$, hence $31 : 1904 = 1 : 61.41$; that is, $\frac{1}{61.41}$ of the amount of iron to which the permanganate solution is equivalent will be the amount of phosphorus to which it is equivalent when titrating yellow precipitate as above, or $61\frac{41}{100}$ times phosphorus $=$ iron.

Two molecules of $KMnO_4$ furnish five atoms of free oxygen on reduction; hence, to furnish 17 atoms of oxygen as above $6\frac{4}{5}$ molecules of permanganate are required which will be the amount equivalent to one atom of phosphorus in the above process.

It is convenient to make the permanganate solution of such a strength that 1 c.c. equals 0.01 per cent. of phosphorus when 1 gram of steel is taken for analysis.

1 c.c. of such a solution must be equivalent to .0001 gram of phosphorus or 1 litre to 0.1 gram.

By the above determined ratios, $6\frac{4}{5}$ molecules of permanganate ($= 158 \times 6\frac{4}{5}$) : 1. atom of P ($= 31$) :: 3.46 grams : 0.1 gram.

Therefore to make the above solution dissolve 3.46 grams of pure crystallized potassium permanganate in 1 litre of water. Allow the solution to stand some time before using.

Finally determine its value exactly, first against pure ammonium ferrous sulphate, and second, against a sample of steel in which the amount of phosphorus has been exactly and repeatedly determined by the magnesia process.

To standardize against the iron salt dissolve 0.8597 grams of the $Fe(NH_4)_2(SO_4)_2 6H_2O$ in 200 c.c. of water containing a little H_2SO_4; add the permanganate solution from a burette until the last drop gives a permanent pink tint and then take the reading.

This amount of the iron salt contains 0.12282 gram of

iron, which will reduce as much permanganate as would be equivalent to .002 gram phosphorus; therefore 20 c.c. of the solution should be required. If more or less is taken, calculate the amount of phosphorus to which 1 c.c. is equivalent by the proportion $n : 20 = .0001 : x$, n being the amount used and x the value sought.

The determination of the value against a known steel is desirable, as it gives a result which is independent of all assumptions as to the nature of the oxide produced by the zinc reduction. The permanganate solution should be carefully protected from dust and other organic matter and only used in burettes with glass stopcocks.

Treatment of the Samples of Iron or Steel. Weigh five grams of steel or one to five grams of iron, according to the percentage of phosphorus, into a 4-in. dish or casserole, and add 25 to 75 c.c. of HNO_3 sp. gr. 1.2. Add the acid cautiously to avoid boiling over. After action has ceased, cover and boil down to dryness, then bake on a hot plate 30 minutes and add 20 to 40 c.c. concentrated HCl. Heat till all the iron oxide is dissolved.

If the metal contains much more than a trace of silicon, evaporate the solution to dryness and dissolve again in the same amount of HCl. Finally, boil down to 15 c.c., being careful to avoid the formation of any dry crusts on the sides of the dish. This is accomplished by keeping the dish well covered and shaking it around a little.

Now add 20 to 40 c.c. concentrated HNO_3, washing off the cover into the dish with it. Boil down again to 10 or 15 c.c. It is essential that no dry iron salt form on the sides. This is easily avoided by covering with an inverted watch glass a little smaller than the dish, so that the condensed acid will flow down the sides and keep them clean. Cool slightly, moving the liquid around so as to dissolve any crusts of ferric nitrate formed. Now add 30 to 50 c.c. of water and filter into a 400 c.c. Erlenmeyer flask. The vol-

ume should be about 75-100 c.c. Steels do not require filtration as a rule, for they leave no residue if low in silicon.

Now add NH_4OH until the ferric hydroxide separates and the mass becomes thick and smells of ammonia. Then add strong HNO_3 gradually until the precipitate redissolves and the liquid has a clear, *amber* color, not the least red. The volume should now be about 250 c.c.; if not, dilute to that amount. Then put a thermometer in the liquid and bring the temperature to 85° C. Now add at once 40 c.c. of molybdic acid solution. Close the flask with a rubber stopper, wrap it in a thick cloth and shake violently for five minutes.

This violent agitation, combined with the high temperature, causes the yellow precipitate to separate promptly and in a particularly dense and easily filtered form.

Finally let settle for a few moments, then uncork the flask and filter off the solution, using a 9 cm. filter. Wash flask and precipitate thoroughly with water containing 1 per cent. of H_2SO_4 and 2 per cent. of $(NH_4)_2SO_4$. Now set the funnel in the flask and dissolve the precipitate back into it with dilute ammonia (1:4) using altogether 30 c.c. To save time some chemists puncture the filter and wash the precipitate through with water. Wash the filter, using as little water as possible.

Finally wash the filter again with ammonia then with water. Now add 80 c.c. of dilute H_2SO_4 (one volume to four of water) to the filtrate and then ten grams of pulverized zinc.

The zinc should be fine enough to pass a 20-mesh sieve and must be as free as possible from iron. The very pure zinc now furnished for this process will sometimes act very slowly. To make it act promptly it should first be platinized as follows:

Treat a quantity of the zinc with water, slightly acidulated with H_2SO_4 and containing a few drops of a solution of $PtCl_4$. After the reaction has proceeded a few minutes, pour off the liquid and wash the zinc thoroughly with water; dry it and preserve it in a

glass stoppered bottle. The almost infinitesimal trace of platinum precipitated on the zinc by this treatment causes the evolution of hydrogen to be rapid and powerfully reducing on the MoO_3.

Now warm till rapid effervescence ensues and heat gently *ten minutes*. At the end of this time reduction will be complete. Meanwhile fold a 12 cm. filter in "ribs;" put it in a funnel, and as soon as the reduction of the MoO_3 is complete pour the liquid off from the residue of the zinc into the filter, collecting the filtrate in a white dish. Rinse the flask and zinc once with water and pour this on the filter after the solution has run through. Then fill the filter with water and let it run through. Thin filter paper must be used so that the whole operation of filtration and washing the zinc shall occupy but three or four minutes.

Instead of filter paper absorbent cotton may be used, a small plug being placed loosely in the neck of the funnel. This should be moistened and the solution poured directly on to it. This will filter very rapidly and satisfactorily.

Now run the permanganate into the dark colored filtrate till the color is discharged, and the last drop gives a faint pink tint, marking the end of the reaction.

There is always some impurity in the zinc, hence it is essential, to make a *blank test*, using the 30 c.c. of NH_4OH, the 10 grams of zinc and 80 c.c. of sulphuric acid as before, but omitting the yellow precipitate. The filtrate in this test will always consume a small amount of permanganate, which must be determined, and deducted from the amount taken in the regular determination, the difference being the permanganate solution equivalent to the yellow precipitate.

The number of cubic centimeters of permanganate solution used, after correction for error of standard, divided by the number of grams of metal taken will give the amount of phosphorus in hundredths of one per cent.

In working this process it is important to check it from time to time upon material similar to that to be analyzed, and in which the phosphorus has been determined gravimetrically.

THE EMMERTON METHOD WITH WET OXIDATION.

By substituting wet methods of oxidation for the baking in the regular process and using the reductor for reducing the molybdic acid, the Emmerton method becomes extremely rapid. It then depends upon such nice adjustment of conditions, however, that it should be especially tested for any variation in the material treated. The permanganate in these processes should be standardized against a steel of approximately the same phosphorus content as that to be analyzed. This is desirable not only on account of the uncertainty in the reduction product but also on account of the fact that the completeness of precipitation of the phosphorus by the molybdic acid solution depends somewhat on the treatment and also upon the percentage of phosphorus in the steel. For example, if a steel containing only .04 per cent of phosphorus were used to standardize the permanganate and the method of precipitation left .001 per cent of phosphorus in the solution it is obvious that while the permanganate so standardized would give satisfactory results on another steel of about the same phosphorus content it would give entirely false results on a steel containing several times as much phosphorus, as the ratio between the phosphorus remaining in solution and that precipitated would be entirely different. Any change in the routine of the precipitation of the phosphorus will also obviously require a restandardization of the permanganate.

By using nitric acid of sp. gr. 1.13 as a solvent the separation of SiO_2 is prevented and filtration is rendered unnecessary.

PROCESS FOR STEELS.

Dissolve 2 grams of the well mixed drillings placed in a 300 c.c. Erlenmeyer flask in 70 c.c. of HNO_3 sp. gr. 1.13 (made by mixing 4 parts of concentrated HNO_3 and 9 parts of water). Heat to boiling to expel most of the nitric oxide, then add in two or three portions 8 to 10 c.c. of a solution of $KMnO_4$, 12 grams to the litre. Boil till the pink color disappears then add a solution of $FeSO_4$ drop by drop till the brown precipitate of MnO_2 is redissolved and the solution becomes clear.

Add NH_4OH to neutralize the greater part of the free HNO_3 which will be the case when the amber color disappears and the solution grows red, then add sufficient HNO_3

to bring back the amber color. Dilute to 150 c.c., heat to 80°C. and add 50 c.c. of molybdic acid solution. Agitate for five minutes by shaking or by blowing a current of air through the solution. Allow to stand for two or three minutes or longer if necessary to settle the precipitate, and filter, washing the precipitate well with 2 per cent. H_2SO_4. Set the funnel in the flask in which the precipitation was made and dissolve the precipitate on the filter in NH_4OH (1:4) using altogether 20 c.c.; then wash the filter well with water. Add 50 c c. of H_2SO_4 (1:4), dilute to 150–200 c.c. and reduce either by adding 10 grams of pulverized zinc and heating for ten minutes as in the Emmerton method, or by passing the dilute solution (200 c.c.) through the zinc reductor as described in the iron assay.

Titrate the reduced solution with $KMnO_4$ till a faint pink remains, not disappearing within a minute. Calculate the percentage of phosphorus from the strength of the $KMnO_4$ solution and the number of c.c. used.

The ferrous sulphate must be free from phosphorus. Pure sodium nitrite or a little sugar may be used instead of ferrous sulphate. These reagents are more easily obtained free from phosphorus.

After having made a few analyses and having determined the proper amount of NH_4OH necessary to add in neutralizing the excess of HNO_3, time may be saved by adding this amount at once, and avoiding the working back with HNO_3. The solution is then shaken till the precipitate redissolves, diluted to 150 c.c., cooled or warmed to 80° and the phosphorus precipitated by molybdic acid solution.

This addition of the proper amount of NH_4OH is not only quicker but gives more satisfactory results than by determining the proper acidity of the solution each time by the depth of the amber color, since this color varies with the sample of steel, the amount of sample taken, and the volume and temperature of the solution.

The yellow precipitate must be washed free from iron salts or the results will be incorrect, since the iron if washed into the flask with the precipitate, will dissolve in the acid and be reduced

by the zinc, finally consuming $KMnO_4$ and causing the results to be high.

Run blanks on the zinc or on the reductor and correct the amount of permanganate used accordingly. Use the same care to filter rapidly and in washing as in the regular Emmerton process.

In using the reductor remember to keep the zinc covered with the liquid during the process and to follow the solution with 100 c.c. of 5 per cent. H_2SO_4 then with 150 c.c. of water. Apply such suction as to cause the liquid to run through in from two to three minutes, not more rapidly, or reduction may be incomplete.

References on Rapid Phosphorus Methods:

Drown. Trans. Inst. Min. Engrs., vol. XVIII, p. 90—uses permanganate and HNO_3 of sp. gr., 1.135 which dissolves silica. Does not evaporate to dryness.

Shimer. Trans. Inst. Min. Engrs., vol. XVII, p. 100—uses permanganate with sulphuric acid. Evaporating until the HNO_3 is expelled.

Clemens Jones. Trans. Inst. Min. Engrs., vol. XVIII, p. 705—uses the method of Drown, but slightly modified, also washes the yellow precipitate with $(NH_4)_2 SO_4$ solution to avoid the presence of nitrates.

Babbitt. Jour. An. and App. Chem., vol. VII, p. 165—advocates the temperature of 25°C instead of 85°, to prevent the precipitation of arsenic.

Clemens Jones. Jour.Trans. Inst. Min. Engs.. vol. 17, p. 411—performs the reduction of the MoO_3 by filtration through zinc.

Dudley and Pease. Jour. Am. Chem. Soc., 1893, p. 519. Standard Methods for Phosphorus on P. R. R.

Doolittle. Jour. Am. Chem. Soc.,1894, p. 234. Discussion of Dudley's paper.

Mahan. Jour. Am. Chem. Soc., 1898, pp. 429 and 792.

Spuller. Zeits. Anal. Chem., vol. 32, p. 538.

See also Methods for the Analysis of Ores, Pig Irons and Steel, Pittsburg, Pa., edited by Phillips, 2d edition.

Titration Process for Ores.—These should be dissolved in HCl. Care must be taken to destroy all organic matter, as this may adhere to the yellow precipitate and cause reduction of the permanganate.

Evaporate the HCl solution with HNO_3, bake and then follow Emmerton. The writer's experience has been that, while good results were obtained with many ores, with some the process seemed to fail.

In low phosphorus ores the traces of phosphorus left in the insoluble residue become important and it must be fused with Na_2CO_3. Disintegrate the "melt" in water, acidify with HCl, boil, precipitate with NH_4OH, wash twice by decantation; redissolve the precipitate in HCl and add it to the original ore solution, then proceed as usual.

TITRATION OF THE "YELLOW PRECIPITATE" WITH STANDARD ALKALI.

This method of determining the MoO_3 in the yellow precipi-

tate avoids the reduction and the consequent uncertainty as to the oxide produced. It has grown rapidly in favor since its introduction.

The reaction may be written as follows:

$$12\ MoO_3,(NH_4)_3PO_4 + 23\ NaOH = 11\ Na_2MoO_4 + (NH_4)_2MoO_4 + Na(NH_4)HPO_4 + 11\ H_2O.$$
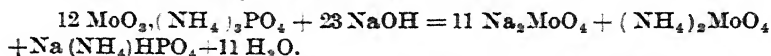
Hundeshagen having shown that 23 molecules of NaOH are required to neutralize 1 molecule of yellow precipitate. This gives a ratio of 1 atom of phosphorus to 23 molecules of NaOH or by weight 31 of P to 921.15 of NaOH, or 1 : 29.71. The alkali solution must be free from carbonate which would interfere with the end reaction. The best indicator is a dilute alcoholic solution of phenolphthalein. The alkali solution should be standardized on pure yellow precipitate carefully dried to constant weight at 150° C. As this substance is rather hygroscopic. it should be redried every time it is used.

To prepare the yellow precipitate for standardizing, precipitate a dilute solution of Na_2HPO_4 by an excess of molybdic acid solution, first acidifying the phosphate solution with HNO_3. Wash the precipitate carefully with water and dry it as directed. Determine the phosphorus in a portion of it gravimetrically. It should contain 1.63 per cent. of phosphorus.

PREPARATION OF THE SOLUTIONS.

Standard Sodium Hydroxide and Standard Nitric Acid.

One-tenth normal solutions may be used. In this case 1 c.c. NaOH is equal to .00013 gram phosphorus.

It is more convenient to have a solution of such a strength that 1 c.c. equals .0002 phosphorus; then if 2 grams of steel are taken for the analysis, each c.c. of soda solution will be equivalent to .01 per cent. of phosphorus. To make such a solution, proceed as follows:

Dissolve 15.4 grams of NaOH as free as possible from Na_2CO_3 in about 200 c.c. of water. Now add a saturated solution of $Ba(OH)_2$ as long as a precipitate forms. Filter at once from the $BaCO_3$ and dilute to 2 litres. This solution will be a little too strong. Now prepare an approximate HNO_3 solution by diluting 20 c.c. of concentrated HNO_3 to 2 litres. Fill a burette with this acid and titrate it carefully against 10 c.c. of the NaOH solution. Next weigh 0.1226 gram of dry yellow precipitate (equals .002 of P) into a beaker; add 50 c.c. of water and 10 c.c. of the

NaOH solution which should dissolve the precipitate to a perfectly clear solution. Now add three drops of phenolphthalein solution and titrate with the acid till the color vanishes. The difference between the acid required for the NaOH and that required in the second case is the number of c.c. of the HNO_3 equivalent to .002 phosphorus. Now add sufficient water to the dilute nitric acid to make 10 c.c. exactly equal to .002 phosphorus. Repeat the test with the yellow precipitate and soda solution, using double the amount of yellow precipitate and 30 c.c. of soda. If the nitric acid is not exactly right, correct it by further dilution and repeat the test. Finally dilute the soda solution until it is exactly equivalent volume for volume to the nitric acid.

The nitric acid, if preserved in a tightly stoppered bottle, keeps its standard indefinitely, but the soda solution will slowly change on account of absorption of CO_2 by the slight excess of $Ba(OH)_2$ present and must be retested against the acid frequently.

In standarizing the acid and alkali, instead of taking yellow precipitate directly a sample of steel of known phosphorus content may be weighed out and treated as in the regular process. It is well to finally check the solution in this way in all cases.

Phenolphthalein Solution.—Dissolve .2 gram of the indicator in 200 c.c. of 95 per cent. alcohol.

PROCESS FOR STEEL.

Weigh out 2 grams of the well mixed drillings into a 400 c.c. Erlenmeyer flask. Add 70 c.c. HNO_3 sp. gr. 1.13. Heat till the metal is dissolved then add to the boiling solution 7–8 c.c. of a solution of $KMnO_4$, 12 grams to the litre. Boil till the pink color disappears and a precipitate of MnO_2 forms. Then add a little pure ferrous sulphate, sodium nitrite or tartaric acid, and heat till the solution clears. Remove from the lamp, add NH_4OH until the amber color of the solution darkens distinctly and takes a reddish tint.

Then add enough HNO_3 to restore the amber color to the solution. Dilute to 150 c.c., and cool or warm to 80° C. Add 50 c.c. of molybdate solution and shake five minutes. Filter, and wash the flask and the precipitate five to ten times with a neutral solution of KNO_3, 5 grams to the litre. Put the filter containing the precipitate back into the flask in which the precipitation was made, and add to the flask and its contents a measured quantity, usually 10 or 20 c.c., of standard NaOH. Dilute to 50 c.c., add 2 drops of phenolphthalein; shake to disintegrate the filter and dissolve the precipitate, and then titrate the excess of alkali with standard acid. The difference between the number of c.c. of nitric acid equivalent to the soda solution used and that required in the titration will be the nitric acid equivalent to the phosphorus; and if the nitric acid is of correct strength each c.c. will represent .01 per cent. of phosphorus.

The process may be somewhat shortened, as noted before in the Emmerton process, by determining the amount of NH_4OH required to neutralize the excess of acid and adding it at once, thus avoiding the reacidifying with HNO_3. This amount can be easily ascertained after a few trials, noting the amount of NH_4OH used, the amount of HNO_3 required to bring it back, and then determining by trial how much NH_4OH is needed to neutralize the amount of acid so used and deducting it from what was originally added.

In dissolving yellow precipitate by standard alkali always keep the liquid cool and the solutions dilute as ammonia is set free in the reaction and is liable to be lost by volatilization if the liquid is concentrated. This would cause error in the nitric acid titration.

References on the Titration Method:

Jour. An. and App. Chem., vol. VI, p. 82.
Jour. An. and App. Chem., vol. VI, p. 204.
Jour. An. and App. Chem., vol. VI, p. 242.
Zeits. Anal. Chem., vol. XXVIII, p. 171.

Determination of Phosphorus by Measuring the Volume of the Yellow Precipitate.—This method is occasionally used for furnace control in steel plants. It requires a special centrifugal machine and graduated bulbs with small collecting tubes for the precipitate. A description will be found in the Journal of Analytical and Applied Chemistry, volume IV, page 13.

With practice it is possible to estimate small percentages of phosphorus in steel by judging the amount of the yellow precipitate as it collects on the bottom of the ordinary precipitation flask. Such estimation will usually serve the same end as is accomplished by the centrifugal apparatus.

THE DETERMINATION OF SILICON IN IRON.

The metals in which silicon has most frequently to be determined are pig iron, containing from one-half to four or five per cent., "ferrosilicon," containing up to 30 per cent., steel with from traces to one per cent., and wrought iron with small fractions of one per cent.

In all these the silicon is combined as Si, not as SiO_2, though there may be a little SiO_2 included as intermixed slag, especially in wrought iron.

All of these metals are soluble in HNO_3, sp. gr. 1.2, except ferro silicon, the Si being oxidized to SiO_2, which passes wholly or in part into solution. Evaporation of the HNO_3 solution to dryness, baking and re-solution in HCl only partially renders this SiO_2 insoluble, a temperature of 250°C. not causing all the SiO_2 to separate.

To accomplish the complete separation of the SiO_2 by this means it is necessary to evaporate to dryness, bake as in the phosphorus determination, dissolve in HCl, and again *evaporate to complete dryness*, expelling all the HCl. On taking up again in HCl all of the SiO_2 is left insoluble. After dilution the solution may be filtered from the residue of $SiO_2 + C$, which after thorough washing, first with HCl and then with water, may be ignited till the carbon is burned off, and weighed.

The SiO_2 thus obtained is never pure, and must be treated by H_2SO_4 and HFl, or must be fused and the SiO_2 separated from the fusion. (See analysis of limestones.)

Hydrochloric acid or aqua regia may be used to dissolve the metal instead of HNO_3, but they do not attack ordinary iron so rapidly. Finally, solution in H_2SO_4 and evaporation till fumes of H_2SO_4 are given off will cause a complete separation of the SiO_2.

For details of these various methods see—
Blair, Chemical Analysis of Iron, nitric acid method.
Troilius, Notes on the Chemistry of Iron, p. 35, sulphuric acid method.
Also Trans. Inst. Mining Engineers, vol. X, p. 162 et seq and 187 et seq.

When a nitric or hydrochloric acid solution containing silica is evaporated with H_2SO_4 the volatile acids will be expelled, and if the temperature is finally raised to near the boiling point of the concentrated acid, the silica is completely dehydrated and becomes insoluble. Titanic acid if present passes into solution and the silica

thus obtained is pure. The following method, slightly modified from one published by Dr. Drown, depends upon this fact.

Trans. Am. Inst. Min. Engrs., vol. VII, p. 346.

In preparing the drillings for analysis, great care must be taken to keep them free from sand. This is difficult in the case of pig iron, drillings from which should usually be cleaned.

This is easily accomplished by folding a sheet of paper over a magnet, then picking up the metal against the paper. The sand and other foreign particles are left behind. On drawing the magnet away from the paper the drillings will fall off and can be collected on a clean sheet of paper. All the drillings must be gone over and no considerable residue should remain. If much graphite-like substance is separated it may hold silicon belonging to the sample.

The drillings should be fine. Large fragments of metal dissolve slowly and may be left as hard grains in the silica, of course vitiating the result. If these lumps remain, add more acid and heat slowly until they dissolve.

Ferrosilicons may need to be pulverized till they go through bolting cloth before they will dissolve.

In "weighing out" great care must be taken to secure an average of fine and coarse, as these usually differ in percentage of silicon.

To avoid unnecessary calculation it is usually convenient to weigh out the "factor weight" of the metal. SiO_2 contains 0.4702 Si; hence, if that weight in grams is taken for the analysis, each milligram of SiO_2 will indicate one-tenth per cent. In low silicon irons or steel 0.9404 or some other multiple of the factor may be used.

Process for Pig Iron and Steel.—Weigh out 0.9404 gram of pig iron or 4.702 grams of wrought iron or steel. Put into a casserole or dish and cover with a large watch glass. Add carefully 30 c.c. of a cold mixture of 8 parts by volume of concentrated HNO_3, 5 parts of concentrated H_2SO_4 and 17 parts of H_2O (for the pig iron) or 100 c.c. of a mixture of 35 parts of concentrated HNO_3, 15 parts of H_2SO_4 and 50 parts of H_2O (for the steel), or use the three acid mixture given further on.

Warm till action ceases, then boil down rapidly on an iron plate or over the bare flame until the $Fe_2(SO_4)_3$, separates as a white mass; continue the heating until 1 nse

fumes of H_2SO_4 are evolved. These have a peculiar suffocating odor, easily recognized. Their formation indicates the total expulsion of the HNO_3, and this is absolutely necessary in order to make the silica insoluble. In the case of steel low in SiO_2 it is necessary to stir up the mass of ferric sulphate thoroughly or it may include SiO_2 not dehydrated and so cause loss. (Dudley.) There will be danger of "spattering" unless the heating is carefully done, but if the dish is well covered this need cause no loss.

Now let cool, then add 10 c.c. of concentrated HCl and wash off the cover into the dish. Dilute to 150 or 200 c.c., cover, set over a lamp and boil until all $Fe_2(SO_4)_3$ is dissolved. This can be recognized by the disappearance of the silky precipitate in the liquid. Continue the boiling for five minutes, as this will cause the solution to filter more easily. Then wash off the cover, and let the liquid stand until all the SiO_2 settles. Decant the clear liquid through a 7 cm. ashless filter, previously washed out with boiling water. Finally transfer and wash the residue with hot water. When partially washed, drop a little HCl on the filter and residue, then wash again with hot water till the filtrate no longer tastes acid. Without drying transfer the filter to a crucible and ignite, gently at first, finally at high heat, until all the carbon (graphite) is burned and the SiO_2 is white. If this is done in a platinum crucible and over a blast lamp the "burning off" of the carbon need not take more than a few minutes.

It is important that the temperature be low at first, not exceeding a dull red until the paper and the amorphous carbon are burned out, as overheating at first will cause the carbon to lump together and it will then burn very slowly. During the final heating over the blast lamp keep the crucible partly covered. The burning may be hastened by directing a gentle current of oxygen gas into the crucible, but if due care is taken this is not necessary. If oxygen is used

take care not to blow any particles of SiO_2 out of the crucible by forcing in the gas too rapidly.

The weight of the SiO_2 in milligrams divided by two in the first case or by ten in the second gives the silicon in tenths of a per cent.

If the above directions are followed exactly as to the dilution and boiling of the solution there will be no need of a filter pump to secure rapid filtration. Boiling with a large excess of water consolidates the SiO_2 so that it filters easily. The funnels and filter paper should be carefully selected, the former should have long and narrow stems that will fill with the liquid and produce a little suction. The funnel angle should be 60 degrees. A porous ashless paper like the Muncktel "black label" is desirable. The precipitate of SiO_2 has no tendency to run through, so that a dense paper is not necessary.

The filter should be kept full while filtering the solution; as if it is allowed to empty the paper will become clogged.

For pig iron and ferrosilicons the following three acid silicon mixture, may be substituted for that already given, and will be found very efficient:

Water	150 c.c.
Sulphuric acid concentrated	40 c.c.
Nitic acid sp. gr. 1.42...........	80 c.c.
Hydrochloric acid concentrated	60 c.c.

Mix in the order given and preserve for use. 25 c.c. of this mixture is enough for the "factor weight" of pig iron (0.4702 gram). Evaporate to strong fumes of H_2SO_4, cool, add a little concentrated HCl, then add water and boil. With this mixture the silica filters particularly well. With steels where the SiO_2 is in very small amount it is necessary to test its purity. Add a drop of H_2SO_4 to the SiO_2 in the crucible and then a few drops of pure HFl or a few crystals of NH_4Fl. Evaporate to dryness over a low flame, not allowing the liquid to boil, and ignite the residue strongly. The fumes of HFl are very poisonous, so the evaporation must be made under a good hood. The SiO_2 passes off as volatile $SiFl_4$. If any residue remains, weigh it and deduct it from the total weight. The difference is SiO_2.

The following process is sometimes used for furnace control instead of the one just given.

The molten iron is chilled by pouring into water. This makes it very brittle. It is then pulverized in a steel mortar, dissolved in HCl, rapidly evaporated to dryness, taken up in HCl, diluted and

filtered. Without drying, the filter is put into a platinum crucible, ignited in a stream of oxygen and weighed. The time required for this process is said to be twelve minutes.

Determination of Silicon in Ferrosilicon.—This material is not easily attacked by any of the above mixtures. If not too high in silicon, it can usually be dissolved by prolonged boiling with aqua regia, adding fresh acid from time to time. Finally add 25 c.c. of dilute (1:3) H_2SO_4, evaporate until fumes of SO_3 appear, and then finish as in the regular process.

Samples with over 10 per cent. Si and which aqua regia will not dissolve are, according to Williams, best treated by fusing with 6 or 8 times their weight of dry Na_2CO_3. Then proceeding with the fusion, as in the determination of SiO_2 in the insoluble matter of a limestone. The metal must be very finely pulverized and not more than 0.5 gram taken.

Williams.—Trans. Am. Inst. Min. Engrs., vol. XVII, p. 542.

Instead of Na_2CO_3 alone, a mixture of Na_2CO_3 and $NaNO_3$ or Na_2O_2 may be used and the fusion conducted as described on page 51. But these reagents are much more injurious to the platinum than the carbonate, though more fusible and more rapid in their action.

THE DETERMINATION OF MANGANESE.

There are two classes of material to be considered; first, ores, slags and metals high in manganese, such as manganite and ferro manganese containing from 15 to 90 per cent. Second, ordinary iron ores, pig irons and steel, containing from a trace up to about three per cent. of manganese. These call for a somewhat different treatment.

THE ACETATE PROCESS.

This is a standard process. It depends upon the separation of the iron from the manganese as a basic acetate. The precipitate will contain also any alumina, titanic acid and phosphoric acid present in the solution. To get a good separation it is essential that the process be conducted very precisely in respect to certain details.

The reactions are as follows:

When Na_2CO_3 is added to the solution containing $FeCl_3$, $MnCl_2$ and excess of HCl, the free HCl is first neutralized, then the Na_2CO_3 begins to act on the $FeCl_3$, forming what is practically a solution of ferric hydroxide in ferric chloride. It has been shown that one part of ferric chloride will hold in solution in this way as much as ten parts of ferric hydroxide.

This solution is very dark red in color and probably contains a complex compound in which the Cl of the $FeCl_3$ is partly replaced by OH. Upon the addition of sodium or ammonium acetate the Cl remaining in this compound is replaced by the acetic acid radical and sodium or ammonium chloride is formed in the solution. When the solution is heated, this complex substance is dissociated; the iron being completely precipitated as hydroxide retaining only a little acetic acid. This is the so-called basic acetate precipitate. The solution now contains free acetic acid. If exactly the right amount of sodium acetate has been added, the manganese will be left in the solution as $MnCl_2$ and none of it will be found in the precipitate. If too much acetate has been added some manganous acetate may form, which is more easily dissociated and oxidized precipitating MnO_2 in a dydrated condition. In this case some Mn may be retained by the precipitate.

From these facts it is evident that as much sodium carbonate should be added as possible without causing a permanent precipitate, and only enough sodium acetate used to replace the chlorine remaining in combination with the iron.

The dissociation by boiling depends upon hydrolysis, and is only complete in very dilute solution; at least 500 c.c. of water must be present for each gram of $Fe(OH)_3$.

THE ACETATE PROCESS FOR THE DETERMINATION OF MANGANESE IN ORES WITH HIGH PERCENTAGES.

The process depends upon the separation of the iron and alumina as basic acetates, precipitation of the Mn as MnO_2 by bromine, re-solution of the precipitate and determination of the Mn as pyrophosphate.

If bromine water is added to the filtrate from the basic acetate, the Mn is completely precipitated as MnO_2, provided an excess of sodium acetate over that required to convert the $MnCl_2$ into acetate is present.

If ammonium salts are present, the MnO_2 will only separate when the solution is made alkaline and then not completely. The iron solution must contain no *ferrous salt* or a red "brick dust" like, slimy precipitate will form, and the filtrate will be cloudy and deposit iron.

The process is perfectly satisfactory provided all details are carefully followed.

Process for Ores.—Dissolve one-half gram of the ore in 15 c.c. concentrated HCl, dilute and filter as in the iron assay.

Evaporation to dryness is usually unnecessary, few ores containing soluble silicates. When such occur, as in slags, dissolve in dilute acid, evaporate to dryness, add HCl and then water.

If no chlorine is given off when the ore is dissolved, owing to the absence of MnO_2, ferrous iron may be present. In this case add a crystal of $KClO_3$ and boil until all the Cl is expelled.

When the ferric chloride solution is evaporated to dryness in the presence of organic matter, a slight reduction to ferrous salt often occurs; hence, in this case always oxidize the solution after filtration by adding a little $KClO_3$ or HNO_3. The solution must be boiled till all the Cl is expelled or Mn will precipitate with the iron in the subsequent separation.

To the filtrate add a solution of sodium carbonate carefully until a slight permanent precipitate forms. Redissolve this with a few drops of HCl, giving each drop two or three minutes to act, and stopping as soon as the solution clears.

Now dilute to about 300 c.c., add one gram sodium ace-

tate, cover the beaker and boil vigorously till the iron separates. Should it not come down promptly add a solution of Na_2CO_3 drop by drop until the precipitation is complete. The liquid must be distinctly acid when tested by a slip of litmus paper. Let the precipitate settle clear and decant the liquid through a 9 cm. filter, pouring off as closely as possible, add 150 c.c. of boiling water, settle, decant as before, and finally transfer the precipitate and wash once with hot water. Wash it off the filter back into the beaker. Dissolve it in the least possible quantity of HCl and repeat the precipitation exactly as before. Transfer the precipitate to the filter and wash well with *hot water*. Test this precipitate for Mn by fusing a little of it with Na_2CO_3 and $NaNO_3$ on a platinum wire. If not free from Mn a third precipitation will be necessary.

The filtrate will amount to about a litre. It should be perfectly clear and colorless. Concentrate it to about 500 c.c., then add ten grams of sodium acetate and an excess of bromine water. Warm until the MnO_2 has settled and the liquid is clear. Filter onto a 7 cm. filter and wash well with hot water.

Wash the precipitate off the filter into a beaker. Now wash the filter paper with dilute HCl, in which a small crystal of oxalic acid is dissolved, receiving the filtrate in the beaker containing the MnO_2. This will dissolve any MnO_2 adhering to the paper.

Heat the beaker containing the MnO_2 and HCl and add oxalic acid solution drop by drop until the MnO_2 is dissolved.

Now dilute to about 150 c.c. and add NH_4OH until the solution is just distinctly alkaline, putting a small strip of litmus paper in the solution as an indicator. If iron is present a slight precipitate will form. Now drop in acetic acid until the solution is just acid. Boil the solution. If any precipitate of $Fe(OH)_3$ separates, filter it off and wash precipitate and filter with hot water.

Unless this precipitate is light red in color and very small in amount, dissolve it in a few drops of HCl, add H_2O, then NH_4OH, then acetic acid as before. Boil till the precipitate separates and filter into the original solution. This re-solution is essential in most cases, and need delay the work but a few moments. The object of the oxalic acid is to reduce the MnO_2 to MnO, and so make it dissolve quickly. MnO_2 is very slowly attacked by dilute HCl alone.

To the filtrate, now perfectly clear and colorless, add an excess of a solution of microcosmic salt ($NaHNH_4PO_4$, $4 H_2O$). Now heat to boiling, add NH_4OH drop by drop as fast as the precipitate formed by each addition becomes "silky" in appearance, stirring all the time to prevent bumping. When no more precipitate forms add enough NH_4OH to make the solution smell slightly of NH_3, and boil till the precipitate is completely silky and settles quickly. Now cool the liquid and filter. Wash the precipitate with water containing a few drops of NH_4OH. Ignite and weigh as $Mn_2P_2O_7$, containing 0.3873 manganese.

The acetate of soda used must be tested for Mn. If any is found, dissolve the salt in water, add bromine water and boil till all the bromine is expelled. Filter the solution from the MnO_2 thus separated and use it instead of the solid salt.

Process for Spiegel Iron and Ferro Manganese.—Take one-half gram of the powdered metal, dissolve in 10 c.c. HNO_3 sp.gr. 1.2, plus 5 c.c. HCl, evaporate to dryness and "bake," then dissolve in 10 c.c. of concentrated HCl, add a little bromine water (to reoxidize any FeO formed), boil down till all excess of bromine is gone and most of the HCl evaporated. Dilute, filter if necessary and precipitate the iron and determine the Mn as by the method for ores.

Some ores and spiegel irons contain copper and nickel. These will come down with the MnO_2 in part at least. They should be separated by H_2S, which will precipitate Ni. Co. Cu. and Zn., but not Mn from a solution containing a slight excess of acetic acid. This may be done in the original acetate filtrate. The solution must be boiled till all H_2S is expelled before adding bromine.

THE ACETATE PROCESS FOR ORES LOW IN MANGANESE.

In this case it is desirable to work upon larger amounts of mater-

ial. The filtration and washing of a large basic acetate precipitate is very troublesome, and can be avoided by taking an aliquot part of the solution after the precipitate has settled.

The error introduced by neglecting the volume of the precipitate is inappreciable when the percentage of manganese is small.

A single precipitation of the iron is entirely sufficient, provided care be taken to avoid excess of sodium acetate.

Extreme care in measuring the solution, as well as in keeping the temperature constant, is also superfluous when less than three per cent. of manganese is present and the volumes are kept large; 10 c.c. on a litre causing an error of only 0.03 per cent.

The precipitate by bromine is MnO_2. On ignition at moderate temperatures with ample access of air, it changes principally to Mn_3O_4, though the exact nature of the oxide produced varies with the conditions of heating. This precipitate also usually retains small amounts of soda salts. For these reasons the percentage of Mn it contains is always a little uncertain. As the variations are limited to a small percentage of the weight of the precipitate, the results obtained by weighing it directly will be sufficiently accurate for all ordinary work, where but little Mn is present.

Process.—Dissolve four grams of the ore in 30 c.c. concentrated HCl exactly as in the iron assay. If there is any ferrous iron present add about 1 c.c. of HNO_3 to completely convert it to ferric chloride. Boil the solution until the excess of HNO_3 is decomposed and the chlorine expelled. The evaporation need not go so far that insoluble iron salts separate; should such form, add more HCl and heat until they dissolve. Add water, warm and filter from the residue.

Take a large Erlenmeyer flask, one which will hold when quite full 2400 c.c. Dry it, then measure into it exactly 2000 c.c. of water; this should reach up into the narrower portion of the flask. Paste a thin strip of paper on the glass to exactly indicate the level of the liquid. The flask must be set on a level desk, and the place it stands as well as the position of the paper mark noted, so that it can be subsequently returned *to the same position.*

Now transfer the solution of the ore to the flask, and dilute it to about 1700 c.c. Then add a solution of Na_2CO_3 gradually until the liquid begins to grow dark red. Con-

tinue to add the reagent drop by drop, shaking the flask after each addition until the liquid is very dark in color and the precipitate formed redissolves very slowly. The object is to reach a point just short of that at which the iron is precipitated. The operation requires practice. Should the point be overstepped, add a little HCl, and when the liquid becomes clear, neutralize over again; but in this case, in the writer's opinion, the iron precipitate is more likely to contain Mn.

Now add six grams of pure sodium acetate. Set the flask on a hot plate and boil the solution vigorously.

The iron should immediately separate as a bulky, red precipitate. If it fails to do so at once, drop in very cautiously a dilute solution of Na_2CO_3 until the separation is complete. Now boil a few minutes longer, then remove the flask to the place where it stood when it was graduated, placing it in the same position, and fill it exactly to the mark with cold water. Stir the liquid thoroughly with a long rod, then let it settle. As soon as it is clear pour off one litre into a graduated flask. This whole operation can be done so quickly that the liquid will not cool materially.

Filter the measured portion of the liquid. The filtrate should be colorless and distinctly acid to litmus paper.

Concentrate the filtrate to about 500 c.c. Add five grams of sodium acetate and boil. Should any precipitate form filter it off, dissolve it in HCl containing a little oxalic acid, add a solution of Na_2CO_3 until a slight permanent precipitate forms, then acetic acid till just acid. Boil this liquid, filter from any precipitate, and add the filtrate to the main solution.

Finally add bromine water, warm until the MnO_2 settles completely, filter, wash well with hot water, ignite and weigh as Mn_3O_4 containing 0.7205 Mn. Calculate the result on two grams of ore taken.

Should the ore leave but little residue this need not be filtered off, but may go into the flask with the solution. In applying this

process to slags and ores containing decomposable silicates, the HCl solution must be evaporated to dryness, taken up again in HCl, HNO_3 added and boiled off as usual.

If care be taken in the neutralizing no precipitate will form on concentrating the filtrate from the iron and delay will be avoided.

Should the ore contain nickel or copper, these will contaminate the manganese precipitate and the results will be inaccurate. In this case the precipitate of MnO_2 must be redissolved in HCl containing a little sodium sulphite. The solution is boiled till free from SO_2, then cooled and nearly neutralized by Na_2CO_3, a little sodium acetate added and the Ni and Cu precipitated by H_2S. In the filtrate from these sulphides the Mn can be determined either by precipitation with bromine or as phosphate.

The Acetate Process may be Applied to Pig Iron and Steel.—Dissolve 4 grams in 50 c.c. HNO_3 sp. gr. 1.2, add 10 c.c. concentrated HCl. Evaporate to dryness and "bake." Redissolve in 25 c.c. concentrated HCl, add a little HNO_3, boil and proceed as with ores low in manganese. Filtration from the insoluble residue is unnecessary.

References on the Acetate Process :

Blair—The Chemical Analysis of Iron.

Jour. Soc. Chem. Ind., vol. X, p. 101, on the properties of Mn_3O_4.

Trans. Inst. Min. Engrs., vol. X, p. 101.

Sillimans Am. Jour. [11] 44 , p. 216, on the determination as phosphate.

Berichte der Deutch., Chem. Gesel.. 1900, p. 1019.

THE FORD-WILLIAMS METHOD FOR MANGANESE.
SEPARATION OF MANGANESE BY CHLORATES.

When potassium or sodium chlorate is added to a solution of manganese in hot concentrated HNO_3 the manganese is all precipitated as MnO_2. To secure complete and rapid precipitation the chlorate should be added to the boiling hot solution in successive small portions, the HNO_3 must be in large excess and concentrated, HCl must be absent, and there must be at least as much iron as manganese in the solution. The precipitate may be filtered off on an asbestos filter and washed with concentrated HNO_3. MnO_2 is entirely insoluble in cold concentrated HNO_3 provided this contains no lower oxides of nitrogen ("red fumes"); if these are present, that is if the HNO_3 is not *perfectly colorless*, the MnO_2 will be reduced and dissolved.

After washing, the precipitate may be redissolved and the manganese determined gravimetrically as pyrophosphate or volumetrically by measuring the oxidizing power of the MnO_2 on ferrous sulphate or oxalic acid.

The precipitate contains a little iron but is free from other impurities.

When the solution to which the chlorate is added contains any HCl, this is first acted upon and broken up before the MnO_2 will separate, chlorine being driven off and water formed by the oxidation. This will result in weakening the HNO_3, and hence in this case more HNO_3 must be present to prevent too great loss of strength.

The method is especially adapted to the determination of manganese in steels and irons low in silicon and dissolving in HNO_3 without residue.

If SiO_2 is present in the solution it may separate in a gelatinous form which prevents filtration and coats the particles of the precipitate so that they dissolve with difficulty. It should be removed by the addition of a few drops of hydrofluoric acid to the liquid after the precipitation of the MnO_2. Sodium chlorate is preferable to potassium chlorate on account of its greater solubility making it easier to wash out of the precipitate.

The Chlorate Process for Steel Low in Silicon—Precipitation of the MnO_2.—Dissolve 5 grams in 60 c.c. HNO_3 1.2 sp. gr., in a 200 c.c. beaker. Evaporate to 25 c.c., then add 100 c.c. of *colorless concentrated* HNO_3. Set on an iron plate and heat to incipient boiling. Now drop in powdered $NaClO_3$ or $KClO_3$, a little at a time, adding each portion when the effervescence produced by the preceding portion has ceased. By the time 2 to $2\frac{1}{2}$ grams have been added the MnO_2 will have separated as a fine brown powder. Now add $\frac{1}{2}$ gram more of the chlorate and boil gently for 10 minutes. If any SiO_2 is present in the solution, after 3 or 4 minutes boiling add a few drops of pure HFl. Then add 1 gram more of the chlorate and 25 c.c. concentrated HNO_3 and boil 10 minutes longer. Remove from the plate and cool by setting the beaker in water. When the MnO_2 has settled, filter without dilution, through an asbestos filter.[1] Finally transfer the

NOTE. 1. *To Prepare the Asbestos Filter.*—Melt the bottom of a six-inch test tube and draw it out into a narrow tube. Cut off the end and into the long funnel thus formed drop a little disc of platinum foil punched full of holes and fastened to a wire which can run into the funnel stem and hold the foil in place. Then put in a little asbestos which has been boiled with HCl, washed and finally ignited in a platinum crucible. Do not "pack" it in, simply pour on

MnO_2 to the filter and wash beaker and filter with *colorless concentrated* HNO_3 three or four times, or until the filtrate is colorless. This can be done without using more than 15 or 20 c.c., adding only a little each time and letting each portion run through before adding the next. Finally wash with a little cold water. If the HNO_3 is colored by lower oxides of nitrogen (from standing and the action of light), it can be purified by blowing a strong current of air through it until it becomes colorless.

After washing the MnO_2 with cold water till the acid taste is gone from the filtrate, (letting each successive portion of water run entirely through before adding the next, so as to not use in all more than 20 c.c.) wash the asbestos and precipitate back into the beaker (which always has some MnO_2 adhering to it).

Volumetric Determination of the MnO_2.—This process consists in dissolving the MnO_2 in a measured excess of an acid solution of ferrous sulphate of a known strength. Each molecule of MnO_2 changes two molecules of ferrous sulphate to ferric sulphate. The amount of ferrous sulphate remaining is then determined by a standard solution of potassium permanganate. The reactions are as follows :

1. $MnO_2 + 2\,FeSO_4 + 2\,H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2\,H_2O$.
2. $10\,FeSO_4 + 2\,KMnO_4 + 8\,H_2SO_4 = 5\,Fe_2(SO_4)_3 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2O$.
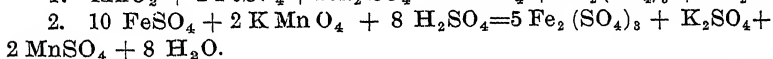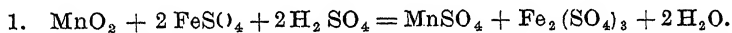
The process requires first, a solution of potassium permanganate of a known strength; second, a solution of ferrous sulphate in dilute sulphuric acid. The strength of this is determined by titration with the permanganate solution.

Preparation of the Permanganate Solution.—Dissolve 1.150 grams of pure $KMnO_4$ in water and dilute to one litre. 1 c.c. of this solution will have the same oxidizing power as 0.001 gram of manganese in the form of the brown precipitate (MnO_2). Check the solution against pure iron or pure ammonium ferrous sulphate $(NH_4)_2Fe(SO_4)_2\,6\,H_2O$. Dissolve 0.1425 gram of the salt in 50 c.c. of water containing 2 c.c. of H_2SO_4. This should consume just 10 c.c. of

the permanganate solution. Run in the solution until the last drop gives a permanent pink color.

If more or less than 10 c.c. is required, calculate the amount of Mn to which each c.c. of the permanganate is equivalent by the proportion.

$.001 : x = $ n $: 10$, n being the number of c.c. of solution used in the test, and x the required value.

Preparation of the Ferrous Sulphate Solution.—Dissolve 20.18 grams of pure crystallized ferrous sulphate ($FeSO_4 7H_2O$) in about 500c.c. of water, to which 25c.c. of concentrated H_2SO_4 has been added, and then dilute to one litre.

Determine its strength against the permanganate solution by measuring 5 c.c. with a pipette into a beaker, adding about 25 c.c. of water and then running in the permanganate till the pink color is permanent. About 10 c.c. should be required. This value must be determined frequently as the solution of ferrous sulphate alters rapidly from the oxidizing action of the air. In a large way it is best kept in a carboy and covered with a layer of kerosene oil to keep out air. The solution can be preserved in this way for some time with but little alteration, and can be drawn out by a siphon as needed.

From the two formulas already given we have the relations between the MnO_2, $FeSO_4$ and $KMnO_4$ as follows:

One atom of Mn in the form of brown precipitate (MnO_2) will oxidize 2 atoms of Fe as ferrous sulphate. Two molecules of permanganate will oxidize 10 atoms of Fe as ferrous sulphate, that is to say two molecules of permanganate will oxidize the same amount of iron as will 5 molecules of MnO_2 containing 5 atoms of manganese. Therefore to find how much $KMnO_4$ will be needed to have the same oxidizing power as 0.001 gram of Mn in the form of the brown precipitate we have the proportion:

Wt. 5 atoms Mn : wt. 2 mol. $KMnO_4 = 275 : 316.3 = .001 : x$, which gives $x = .00115$ gram, the amount of $KMnO_4$ to be dissolved in 1 c.c. if 1 c.c. is to be equivalent to .001 gram Mn as "brown precipitate." This is 1.15 gram in a litre.

To determine the amount of iron, or of ammonium ferrous sulphate to which 1c.c. is equivalent, we have:

Wt. 1 atom Mn : wt. 2 atoms Fe = 55 : 112 = .001 : x, in which x is the required amount of iron. The value of x is 0.002034. To determine the amount of the ammonium ferrous sulphate, as this contains $\frac{1}{7}$ of its weight of iron, multiply the value of x by seven ∴ = .01425 for 1 c.c., or the figure given in the directions for 10 c.c.

That 5 c.c. of the ferrous sulphate solution may be equivalent to 10 c.c. of the permanganate it must contain 0.02034 Fe. This corresponds to 20.18 grams of $FeSO_4, 7H_2O$ to the litre.

Determination of the MnO_2.—To the asbestos and MnO_2 in the beaker, add the solution of ferrous sulphate from a pipette 5 c.c. at a time until, after stirring and warming, the MnO_2 is *completely* dissolved. It is best to take the same pipette used in standardizing. Break up all lumps of asbestos and precipitate with a glass rod as they may conceal undissolved particles of MnO_2. Now add a little water and run in the permanganate solution till a pink color is produced, not disappearing under two or three minutes. Read the burette and deduct the amount used from that to which the amount of ferrous sulphate taken would have been equivalent; the difference is equivalent to the Mn present in the precipitate. This, corrected by the factor for the permanganate solution, will give the amount of Mn in milligrams.

As an example—Suppose that 5 c.c. of ferrous sulphate solution equaled 9.6 c.c. of permanganate solution, and 10.3 c.c. permanganate equaled 0.1425 grams of ammonium ferrous sulphate. If 15 c.c. of ferrous sulphate solution were added to dissolve the MnO_2 and the permanganate required to oxidize the excess was 4.5 c.c., then the calculation is as follows:

$3 \times 9.6 = 28.8$ = the permanganate equivalent to the $FeSO_4$ used.

4.5 = the "titre back."

24.3 = the number of c.c. of permanganate equivalent to the precipitate.

$24.3 : x = 10.3 : 10$ (x being the true amount of correct permanganate).

$x = 23.6 = 0.0236$ gram Mn in the precipitate.

THE CHLORATE PROCESS FOR ORES.

ake 5 grams: Dissolve in 50 c.c. of concentrated HCl. Evaporate

to dryness, avoiding a temperature above 100°; add 20 c.c. HCl, and then water. When dissolved, filter into a No. 2 beaker. Add 50 c.c. concentrated HNO_3, evaporate to a syrup, then add 100 c.c. of concentrated HNO_3 and proceed as before.

THE CHLORATE PROCESS FOR PIG IRON.

Dissolve 5 grams of the metal in HNO_3 sp. gr. 1.2, taking about 60 c.c. Then add 25 c.c. HCl, evaporate to dryness and bake. Dissolve in HCl, filter from the SiO_2, and to the filtrate add 0.2 gram ammonium fluoride or a few drops of hydrofluoric acid. Then add 50 c.c. of HNO_3. Concentrate to a syrup, add 100 c.c. HNO_3 and proceed as before. The hydrofluoric acid expels traces of SiO_2 from the solution and greatly accelerates the filtration from the MnO_2. (E. F. Wood.)

The above process, carefully conducted, is capable of giving very accurate results, but it requires practice and should be tried on metals in which the Mn has been carefully determined by the acetate method until the two give concordant results.

For Ferro Manganese and Ores high in Manganese.—The permanganate solution should be standardized by working on a metal of known percentage of Mn, as the composition of the precipitate is considered by some chemists not to be exactly MnO_2, but by thus standardizing in the same way that the ore is analyzed, all risk from this source is avoided. Where only small amounts of Mn are present this source of error is unimportant.

The acetate process, however, is better adapted to high manganese materials, and if skillfully worked is nearly as rapid as the other if HCl has to be expelled by evaporation with HNO_3.

One slight objection to the chlorate process is the large amounts of expensive acids required.

To avoid this the process can be worked on smaller amounts of substance, but great care and skill are then needed to secure close results. All measurements and titrations must be very exact.

Take one gram of iron or steel, dissolve it in 15 c.c. of HNO_3 sp. gr. 1.2. Evaporate to 10 c.c., add 35 c.c. HNO_3, and after precipitation and boiling, 10 c.c. more, reduce the $KClO_3$ to about one gram, filter, wash and proceed with the volumetric determination of the precipitate.

It is possible to determine the MnO_2 in the presence of the nitric acid without filtering it off by proceeding as follows. After precipitating the MnO_2 cool the acid and dilute it to about 400 c.c. with cold water. Now add the ferrous sulphate solution to dissolve the MnO_2 directly, and immediately titrate with the permanganate. In working in this way the excess of chloric acid must be completely boiled off before diluting the solution and the temperature of the

liquid kept quite low when adding the ferrous sulphate. Great care in these points is necessary in order not to start the reaction between the HNO_3 and the $FeSO_4$ which would vitiate the results. The permanganate solution should be standardized under similar conditions.

Trans. Am. Inst. Min. Engs. vol. IX, p. 397.
"   "   "   "   "   " X, p. 100.
"   "   "   "   "   " XII, p. 73.
"   "   "   "   "   " XIV, p. 372.
Jour. Am. Chem. Soc. 1898, p. 504.
Am. Jour. Sci. 5 (4) 260.
Jour. An. App. Chem. vol. II, p. 249.

VOLHARD'S PROCESS FOR MANGANESE.

This is a volumetric process depending upon the reaction between potassium permanganate and manganous salts by which all the manganese is precipitated as MnO_2.

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + 2KHSO_4 + H_2SO_4.$$
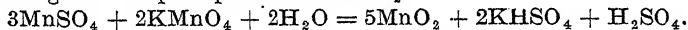
The solution must be neutral or very nearly so. The titration must be made with the solution nearly at the boiling point and very dilute or the precipitate will not settle quickly, and it will be difficult to see the end reaction. For the same reason the solution must be vigorously shaken or stirred and the permanganate added rather slowly, especially at first. Too rapid addition of the permanganate will cause the MnO_2 to precipitate on the glass, forming a firmly adherent yellowish brown stain which makes it very difficult to see the final pink color produced by the excess of permanganate when the titration is finished.

The permanganate solution used in the iron assay will serve for manganese. If 1 c.c. equals 0.01 Fe, then 1 c.c. will equal .002946 Mn.

In this process the iron is separated from the manganese by means of zinc oxide. ZnO precipitates the iron completely as hydroxide from a dilute solution of ferric sulphate, while manganese sulphate is not affected and remains in the solution.

Sufficient ZnO must be added to neutralize any free sulphuric acid present as well as to precipitate the iron.

PROCESS FOR ORES.

Take 0.5 gram of the sample; ignite it to redness if carbonaceous matter is present; then transfer it to a casserole and digest with 15 c.c. of concentrated HCl. If any ferrous iron is present add a few small crystals of $KClO_3$ to oxidise it to the ferric state. Finally boil until all free Cl is expelled. Now add 10 c.c. of dilute H_2SO_4 (1:1) and evaporate till

fumes of H_2SO_4 begin to come off, then cool the casserole and add 75 c.c. of water. Warm till all of the ferric sulphate goes into solution and then transfer to a 200 c.c. graduated flask.

Add a solution of Na_2CO_3 to the contents of the flask until most of the free acid is neutralized. Now cool the contents of the flask if at all warm and then add ZnO suspended in water, small portions at a time and shaking after each addition, till the iron separates as hydroxide. Dilute to 200 c.c. and mix thoroughly. Let the precipitate settle and then filter through a dry filter. Collect 100 c.c. of the filtrate rejecting the first few cubic centimeters that run through. Transfer this portion to a large flask, dilute it to 300 c.c., add exactly two drops of HNO_3 sp. gr. 1.2 and heat to boiling. Titrate with $KMnO_4$ shaking well after each addition, till a faint pink remains, which does not disappear for a few minutes. From the strength of the $KMnO_4$ and the number of c.c. required, calculate the percentage of Mn.

The titration must be made rapidly so that it will be finished before the solution cools. If by accident the solution cools so that the MnO_2 separates badly before finishing the titration, heat it again quickly but not to boiling.

Run a blank on the reagents to test them for manganese or any other substance which would reduce the $KMnO_4$ solution.

PROCESS FOR PIG IRON AND STEEL.

Weigh out 1 gram of the well mixed borings into a casserole. Add gradually 25 c.c. of HNO_3 sp. gr. 1.2. When the metal is dissolved evaporate to dryness and bake for a few minutes, then take up in 10 or 15 c.c. of HCl and heat till the iron salts go into solution. Now add 10 c.c. of dilute H_2SO_4 (1:1) and evaporate till dense fumes of H_2SO_4 are given off, keeping the dish well covered, to avoid loss from spattering, and to avoid the formation of dry salts on the sides of the casserole. Cool, add 100 c.c. of water, and warm till all the ferric sulphate goes into solution. Transfer to a 500 c.c. flask, nearly neutralize with Na_2CO_3, cool and

then add the zinc oxide, suspended in water as described before, till the iron is precipitated. Dilute to 500 c.c. mixing the contents of the flask thoroughly. Filter off 250 c.c. Add to this two drops of HNO_3 sp. gr. 1.2, heat to boiling and titrate carefully with $KMnO_4$ till a faint pink color is permanent.

Where the amount of manganese in the sample is less than seven or eight-tenths per cent. the process is not satisfactory, unless more of the sample is taken, since the precipitate will not clot and settle properly if there is less than five or six milligrams of manganese in the liquid. Therefore, in applying the process to ores or metals quite low in manganese, enough sample must be weighed out so that there shall be at least this amount of manganese in the liquid titrated.

As more than a trace of free acid interferes with the titration, the amount of HNO_3 added must not exceed that indicated or the precipitate will settle badly and the end point be indistinct. Evaporation with H_2SO_4 is necessary to destroy the carbonaceous matter as well as to expel the HNO_3, both of which may affect the titration.

Instead of taking one gram for the analysis, it is usually more convenient to take such an amount of the sample as will make one c.c. of the permanganate equivalent to one per cent. of manganese. This amount can be calculated from the iron standard of the permanganate. Thus, if 1 c.c. of the $KMnO_4$ equals .01 Fe, take 0.5892 gram of the sample for the process, then the half of the solution taken for the titration will contain 0.2946 gram of the sample and each c.c. of permanganate used will obviously represent one per cent. of Mn.

For steels low in carbon the Volhard method has been modified by omitting the evaporation with H_2SO_4 and not filtering from the precipitate of ferric hydroxide produced by the ZnO, but instead simply decanting an aliquot part of the somewhat turbid liquid and titrating directly in the presence of the nitrates. In this case the permanganate should be standardized on a steel of similar kind in which the Mn has been determined gravimetrically.

Stone. —Jour. Am. Chem. Soc. 1896, p. 228.
Auchy.— "   "   "   " 1896, p. 498.

COLOR PROCESS FOR MANGANESE.

When a solution of manganese in dilute HNO_3 is boiled with PbO_2 permanganic acid is formed, coloring the solution purple.

The depth of this color increases with the amount of manganese present, and by comparing it with that produced in the same way in a solution containing a known amount of manganese, that present in the first solution can be estimated. The method is sufficiently accurate for technical purposes, and can be applied to steels, pig irons, and ores, in which the per cent. of manganese is small.

A standard is required containing a known amount of Mn. This standard should be of precisely the same kind of material as that to be analyzed; steel being used for steel, iron for iron, ore for ore, etc.

The PbO_2 must be free from Mn.

While the method is most commonly applied to steel, it is applicable with slight modifications to the other materials mentioned.

As the depth and shade of color produced is influenced by the time of heating, the strength of the acid, and the volume of the liquid, it is essential that the standard and the sample be treated in exactly the same manner, and that the standard be near the sample in percentage of Mn. The process can be conducted in test tubes or in small flasks. The boiling should be gentle but continuous, and so regulated as to cause equal concentration of the liquid in standard and sample.

PROCESS FOR STEEL.

Weigh 0.2 gram of the steel into a 50 c.c. CO_2 flask. Add 15 c.c. of HNO_3 sp. gr. 1.2. Close the mouth of the flask with a small glass bulb; heat carefully on a hot plate or steam bath until the iron is all dissolved. Transfer to a 100 c.c. flask, filtering, if necessary, and dilute to 100 c.c. Mix thoroughly. Now put 10 c.c. of the solution into a small flask, add 3 c.c. of HNO_3, sp. gr. 1.2 and heat carefully on a hot plate. As soon as the solution is hot, but before it begins to boil, drop in a very little PbO_2, and when the solution begins to boil, add 0.5 gram more PbO_2. Close the flask with the bulb and keep the solution boiling gently but continuously for exactly five minutes. Now set the flask in cold water until the PbO_2 settles to the bottom and the violet liquid is absolutely clear. Avoid exposure to bright light which may cause the color to change. A solution of the standard steel should be prepared and treated in the same way and at the same time.

Pour off the two solutions into two graduated tubes and dilute the darker till the colors match when compared over a sheet of white paper. The volumes will then have the same ratio as the amounts of Mn in the standard and test sample.

Small flasks used in this way and kept closed with glass bulbs are as satisfactory as the special calcium chloride bath and test tubes sometimes used. The heavy lead precipitate settles so completely to the bottom that with care the liquid can nearly all be poured off without disturbing it. Where the standard and the sample are close in Mn percentage, the small amount of liquid left in each flask will not appreciably affect the results if the original volumes were about equal. Eight inch test tubes may be used instead of the flasks. They can be heated in a calcium chloride bath at 115° C, or on a sand bath provided with a wire rack for holding the tubes.

The PbO_2 settles a little better in the tubes, which should be placed upright in cold water. If a centrifugal machine is available, (such for instance as is used for separating the phosphorus precipitate for measuring in the Goetz process), the PbO_2 can be rapidly separated by pouring the contents of the flasks into test tubes and whirling them in the machine.

The addition of a little PbO_2 before the boiling commences causes this to start off quietly, and on adding the rest of the reagent there is no violent action such as is likely to take place if the oxide is added at once to the boiling liquid and which may throw liquid out of the flask.

When the Mn is very low 25 c.c. of the solution of the steel may be used instead of the 10 c.c. directed, provided the amount of HNO_3 is proportionately increased.

Dilution and division of the solution as directed is desirable, where the amount of Mn is sufficient to give a deep color. It is unnecessary in low Mn steel. In this case proceed as follows:

Dissolve 0.2 gram of the steel in 15 c.c. HNO_3 1.2 sp. gr. Boil till nitrous fumes are expelled and add 15 c.c. of water, then add the PbO_2 and boil as before directed. Allow to settle, decant off and compare. Use care to heat the standard and sample equally, both during the solution and after adding the PbO_2. Instead of dissolving the standard each time a test is made, a quantity may be dissolved and the solution then diluted so that 10 c.c. corresponds to the weight of the sample taken in the test. This volume may then be taken for comparison with each set of tests. Thus for the first process where the solution is diluted and divided, dissolve 2 grams

of the standard steel, dilute to one litre and use 10 c.c. each time for comparison.

For steels of moderate percentage of manganese the time of boiling may be shortened to three minutes.

PROCESS FOR PIG IRON.

Dissolve 0.2 gram in 10 c.c. HNO_3, sp. gr. 1.2. Add one-half c.c. HCl and boil down to one or two c.c. Add 10 c.c. concentrated HNO_3 and boil down one-half. Now dilute to 100 c.c., filter through a dry filter, take an aliquot part of the filtrate and proceed as in the regular process. Use a pig iron standard. With very low Mn or coarse-grained iron it may be desirable to take larger amounts to secure an average. In this case use 1 gram and dilute to 100 or 500 c.c. according to the amount of Mn present.

PROCESS FOR ORES.

Dissolve 0.2 gram in 5 c.c. of HCl. Boil down to a syrup; add 10 c.c. of concentrated HNO_3, evaporate again to a syrup. Add 10 c.c. of HNO_3, 1.2 sp. gr. dilute, filter and proceed as with pig iron, using an ore standard.

Hunt.—Am. Inst. Min. Engs. vol. 15, p. 164.

COLOR METHOD USING AMMONIUM PERSULPHATE.

This method is due to Marshal and Walters. See Chemical News, Feb. 15, and Nov. 15, 1901. It depends upon the fact that if ammonium persulphate (NH_4SO_4) is added to a solution of manganese in dilute nitric or sulphuric acid, it will, on warming, promptly and completely oxidize the Mn. to permanganic acid, provided a small amount of silver nitrate is present. The silver salt is essential, for if not present the manganese will be precipitated as MnO_2. If too much silver salt is present, silver peroxide will precipitate and make the solution muddy.

The solution should not be boiled, but merely warmed until the color develops.

It is said that the persulphate should be slightly damp, but we have used this salt dried in a dessicator with satisfactory results.

WALTER'S PROCESS FOR STEEL.

Dissolve 0.1 or 0.2 gram of the steel, according to the percentage of manganese, in 10 c.c. of HNO_3, sp. gr. 1.2. Heat until all nitrous fumes are driven off. Now add 15 c.c. of a solution of silver nitrate containing 1.33 grams of

the salt to 1 litre of water. This will cool the solution considerably. Now immediately add about 1 gram of ammonium persulphate, and warm until the color commences to develop, and then for about a half minute longer. Remove from the heat and set it in cold water while the evolution of oxygen continues. As soon as the solution is cool, compare it with a solution of standard steel treated in the same manner.

The solution of the standard steel may be prepared in quantity, as noted before, by dissolving several grams of the metal in a sufficient amount of nitric acid, sp. gr. 1.2, and diluting with the same strength acid until 10 c.c. of the solution contain 0.2 gram of steel. Ten c.c. of this solution are then used with each set of determinations.

THE DETERMINATION OF SULPHUR.

Sulphur occurs in iron ores as sulphides, such as pyrite (FeS_2) and sphalerite (ZnS) and also as sulphates, such as gypsum ($CaSO_4$, $2H_2O$), barite ($BaSO_4$) and celestite ($SrSO_4$). In iron and steel it occurs as sulphide only. In the gravimetric methods for determining sulphur it is first converted into some soluble sulphate and then the sulphuric acid precipitated by barium chloride and weighed as barium sulphate.

DIRECT OXIDATION METHODS.

Conversion of the Sulphides to Sulphates.—All sulphides are completely oxidized to sulphates when fused with a mixture of dry Na_2CO_3 and $NaNO_3$ or with Na_2O_2 (sodium peroxide.

As free sulphur and certain disulphides give off sulphur vapor at a comparatively low temperature (below the fusing point of Na_2CO_3), when these are present care must be taken to prevent loss by the escape of this vapor. The mixture of ore and flux must be covered with a layer of the pure "fusion mixture" and heated carefully.

After fusion all the sulphur, whether originally present as sulphide or sulphate (even in $BaSO_4$) will be found as Na_2SO_4, the bases present remaining as oxides or carbonates. When the fused mass is boiled with water till thoroughly disintegrated and then filtered off and washed, the sulphate all passes into the filtrate.

Sulphides can be more or less completely oxidized to sulphates in the "wet way" by treating them with hot concentrated HNO_3 or aqua regia. Wet methods are not very satisfactory, as free sulphur is liable to separate and fuse to globules, its melting point being below the boiling point of HNO_3. Once in this form it is very slowly oxidized by boiling with ordinary oxidizing agents. Iron sulphide can be completely oxidized however by heating with a large excess of concentrated HNO_3 and adding a little powdered $KClO_3$.

When iron sulphide, or even iron containing but little sulphur, is dissolved in dilute HNO_3 1.2 sp. gr., a considerable proportion of the sulphur separates as such and escapes oxidation.

Solutions containing ferric sulphate, on evaporation to dryness and "baking," as is common in iron analysis, may loose SO_3 unless enough potassium or sodium is added to hold it all in combination with the alkali, as the sulphate of iron is easily decomposed by heat and SO_3 expelled.

See Fresenius—Quantitative Analysis; also
Phillips. Jour. Am. Chem. Soc. 1896. Page 1079.

The Precipitation of SO_3 by $BaCl_2$.

This precipitation must be conducted under carefully regulated conditions, if the results are to be satisfactory.

Barium sulphate, while entirely insoluble in water, is not so in dilute acids, the amount dissolved increasing with the concentration of the acid. The presence of a considerable excess of $BaCl_2$ in the liquid appears, however, to counteract this solvent action. Thus a sufficient *excess* of $BaCl_2$ will completely precipitate the sulphuric acid from a solution quite strongly acidified with HCl.

When $BaSO_4$ is precipitated in solutions containing much iron, unless the solution contains a considerable excess of HCl, basic iron salts will adhere to the precipitate, making it reddish in color. This color is best seen after the precipitate is ignited. Some of the sulphuric acid appears to be in combination with the iron instead of with the barium and is driven off on ignition, leaving ferric oxide; so that these impure precipitates are liable to give *low results*, particularly if subsequently purified and the $BaSO_4$ present determined. Water alone will not wash the iron out of such an impure precipitate. The iron can be dissolved out of the precipitate by concentrated HCl, but this will dissolve some of the $BaSO_4$. If, however, the HCl is mixed with a solution of $BaCl_2$, its solvent action on the precipitate is reduced to practically nothing. A mixture of 10 c.c. of concentrated HCl, 10 c.c. of 10 per cent. $BaCl_2$ solution and water enough to dissolve the $BaCl_2$ precipitated by the acid, gives a wash that can be safely used to free a barium sulphate precipitate from a little iron. The precipitate must be subsequently washed thoroughly with water.

Barium salts, particularly the nitrate, have a strong tendency to adhere to the precipitate, making it impure. These cannot be completely washed out with water.

Acid solutions of $FeCl_3$ when hot, hold a little $BaSO_4$ in solution; this separates completely when the liquid cools. The precipitate of $BaSO_4$ is fine, liable to run through the filter and impure, when precipitated cold, or in concentrated solutions or by *too concentrated a solution of $BaCl_2$*. This is important when much SO_3 is present. The solution of $BaCl_2$ must then be *well diluted* and heated to boiling before being added. In this way there is obtained a granular, rapidly subsiding precipitate easy to wash and *pure*.

If the $BaSO_4$ precipitate is too fine and settles slowly, set the beaker containing the slightly acid liquid and the precipitate on a warm plate and keep it at a temperature a little short of boiling for some time, stirring up the precipitate occasionally. Treated in this way the precipitate will gradually grow dense and granular so that it can be easily filtered.

METHOD FOR SULPHUR IN IRON ORES

Mix 1 gram of the finely pulverized ore with 8 grams of dry Na_2CO_3 and 0.5 to 1 gram of $NaNO_3$, according to the amount of sulphur in the ore. Put the mixture in a platinum crucible and fuse carefully. As soon as it is well melted chill the crucible by dipping the bottom into water. This will usually loosen the cake so that it can be removed from the crucible.

As ordinary gas contains sulphur, fusions made over it are likely to absorb some SO_2 from the flame. Therefore an alcohol or gasolene blast lamp should be used. If gas is used, the crucible must be kept covered during the fusion and should be protected by inserting it into a tightly fitting collar of sheet asbestos up to near the top. This will act as a shield to prevent the products of combustion from getting into the crucible. In accurate work it is always necessary to make a blank analysis, and determine the small amount of sulphur contained in the reagents or absorbed from the gas flames. Deduct this from the amount found when working on the ore.

Boil out the fusion with water until all the material is soft and no hard lumps remain. If the solution is colored by Na_2MnO_4, add a few drops of alcohol. Filter and wash well with hot water. Add HCl to the filtrate till just acid, evaporate it to dryness carefully, and dry at 100°C. Now add 5 c.c. of HCl first diluted with its own volume of water. Warm and add 50 c.c. of water, heating till everything is dissolved but a little SiO_2. Filter and wash. The filtrate should not exceed 100 c.c.; if it does, concentrate it. Now heat nearly to boiling and add 5 to 10 c.c. of a 10 per cent. solution of $BaCl_2$ previously diluted with 10 to 20 c.c. of water and heated. Stir and let the precipitate of $BaSO_4$ settle. When clear, filter, wash with hot water, ignite and weigh the $BaSO_4$. This weight multiplied by 0.137=S.

$BaSO_4$ is easily reduced to BaS by heating with carbon. This may occur in the crucible and will make the results come low; hence, in igniting the precipitate detach it as far as possible from the filter, burn the paper carefully on a platinum wire, avoiding a high heat. Add the ash to the precipitate in the crucible and heat gently with the cover off until all the carbon is burned, finally igniting to a bright red heat.

Instead of drying the paper, the wet filter and precipitate may be ignited together by proceeding as follows: Put the filter paper containing the precipitate into a good sized platinum crucible. The paper should be put in point down and open, just as it sets in the funnel. Now set the uncovered crucible over a very low flame and dry out the paper carefully. Then continue the heat so as to char the paper without letting it ignite. Should it catch fire, extinguish the flame by momentarily covering the crucible. When all the volatile matter is expelled, slightly increase the heat which should not, however exceed a dull red. The carbon will now all burn away and the precipitate become white. Finally raise the temperature to bright redness. Cool and weigh as before. This process is called "smoking off" the filter and saves much time. It can be used safely on all small $BaSO_4$ precipitates. After weighing the precipitate, add a little water to it and test with turmeric paper. If it reacts alkaline, the results are untrustworthy, as reduction has occured; in this case add a drop of H_2SO_4; heat till dry, ignite and weigh again, taking the second weight as the correct one.

WET OXIDATION METHOD FOR SULPHUR IN ORES.

Weigh 1 to 5 grams of the very finely pulverized ore. Put it in a covered casserole or beaker and add 20 c.c. of concentrated HNO_3. Heat and add 1 gram of $KClO_3$ in several portions. Now digest at a moderate heat till all action ceases, then evaporate off most of the HNO_3. Now add an excess of HCl and warm until the iron is all dissolved. Evaporate to dryness and proceed as with the dried residue in the determination of sulphur in iron or steel.

To determine the Sulphur in Pyrites use from 0.1 to 0.2 gram of the substance, treating it with 25 c.c. of concentrated HNO_3 and 3 grams of $KClO_3$. The potassium chlorate should be tested for sulphur.

This method fails to determine the sulphur in any $BaSO_4$ or PbS contained in the ore. Therefore it is not so generally applicable

as the fusion method unless the insoluble residue is separately treated by the fusion method and any sulphur it contains recovered.

METHOD FOR SULPHUR IN IRON AND STEEL.

As the sulphur is usually present in these metals in very small percentages only, its accurate determination demands great care. Take from 2 to 5 grams according to the percentage of sulphur. Add 25 to 40 c.c. concentrated HNO_3. Cool the dish if the action is too rapid, or heat it if it is too slow. The rate of solution must not be too rapid or low results may follow.

When the metal is nearly all dissolved, heat to boiling and add 2 to 3 c.c. of concentrated HCl to complete the solution. Now add about 0.5 gram $KClO_3$ free from sulphur. Boil to dryness and bake on a hot plate 10 minutes. Add 10 to 20 c.c. concentrated HCl to dissolve the residue and again dry down thoroughly. Dissolve up again in 15 to 40 c.c. of concentrated HCl. Evaporate the solution until a skin begins to form on the surface or until it becomes syrupy. Now add 5 to 10 c.c. of concentrated HCl, according to the amount of iron taken. When all the iron dissolves dilute the liquid with its own volume of hot water and filter into a small beaker through a paper previously washed out with a little hot dilute HCl (this facilitates filtration). Wash the dish and insoluble residue with hot water.

The filtrate and washings must not exceed 75 c.c. Now warm to about 60° C. and add 10 c.c. of a 10 per cent. solution of $BaCl_2$. Let stand till the precipitate settles, leaving the liquid perfectly clear. (Two hours is sufficient if everything is right.)

Filter on to a small ashless filter, wash with water containing a few drops of HCl, ignite and weigh the $BaSO_4$. Test the filtrate by the addition of considerably more $BaCl_2$ solution which must give no additional precipitate.

The residue from which the solution for the determination of sulphur is filtered must contain no basic iron salts, as these may hold sulphur. These are likely to form if the HCl solution is concentrated too far and insufficient acid is added before dilution.

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It is imperatively necessary that a blank be run on all the reagents used in the process and the weight of $BaSO_4$ obtained in this way deducted from that found in the analysis.

Certain high carbon steels and most ferrosilicons will resist the action of concentrated HNO_3 almost entirely. When treating such metals add some potassium chlorate with the nitric acid at the start, and also at intervals add concentrated HCl, 1 c.c. at a time, until the metal is dissolved; then add more $KClO_3$ and proceed as usual.

Ferrosilicons with over 10 per cent. of Si will resist the action of all the ordinary solvents. These and other insoluble alloys cannot be treated by wet methods for the determination of sulphur.

Where the percentage of Si does not exceed about 15 per cent, the addition of sodium fluoride to the HNO_3, as described under Phosphorus on page 51 , will usually bring the metal into solution and the determination can then be carried out as usual, by adding the chlorate, evaporating, baking, and taking up in HCl. In other cases the metal must be fused. The fusion is best made in a platinum crucible with a mixture of equal parts of $NaNO_3$ and Na_2CO_3, using at least 6 parts of the mixture to 1 of the metal. The fusion can be then soaked out with water and the water solution treated as in the case of an ore.

The sulphur will all go in to the water solution, provided the iron is completely oxidized. It is essential that the metal be very finely powdered. The peroxide of sodium can be substituted for the nitrate or may be used alone, in which case at least 8 grams of the reagent must be used for 1 of metal, and the fusion made in a nickel crucible. Blanks must be run on all the reagents.

F. C. Phillips Journal Am. Chem. Soc. 1896. Page 1079.

E. H. Saniter Journal Soc. Chem. Indst. 1896. Page 155.

THE DETERMINATION OF SULPHUR IN PIG IRON AND STEEL

BY EVOLUTION AS H_2S.

The direct oxidation methods are accurate and the only ones that can be relied upon to give with certainty the total sulphur in any material. But they are too slow to answer for control work. For such purposes the evolution methods are very generally used. They are

either gravimetric or volumetric and can be made extremely rapid. For some materials they will give reliable results.

These methods all depend upon the assumption that when iron is dissolved in HCl the whole of the S is evolved as H_2S and passes off with the excess of H. This is probably true or nearly so for steel containing but little carbon and possibly for gray pig iron; it certainly is not true for white iron and mottled irons high in combined carbon; and probably not true for high carbon steels and some ferro-silicons, especially those containing much S.

In these latter materials part of the S appears to be evolved as more or less volatile liquid or possibly gaseous compounds of carbon, hydrogen and sulphur and not as H_2S. The proportion of the S evolved as H_2S will vary in the same iron if the heat treatment has been different; if slowly cooled, it may be gray and evolve most of the S as H_2S; if suddenly cooled by chilling in water (shot samples) it will be white and only a small portion of its S may be evolved as H_2S. Hence by evolution methods the latter sample would show a much lower percentage of sulphur than the former.

If hydrogen gas mixed with these volatile sulphur carbon compounds is passed through a tube of glass or porcelain heated to dull redness, the sulphur compounds are all decomposed and resolved into H_2S. If the tube is filled with asbestos coated with a little platinum black the action is more rapid. If the evolution process is to give reliable results when applied to all classes of iron and steel this treatment of the evolved gas is essential. Care must be taken to exclude all air or explosions may result. The residue left after the solution of the iron consists largely of carbon and silica but sometimes contains sulphur and should be filtered off and tested by the oxidation method unless previous experience with the particular kind of material has shown that it leaves a residue free from sulphur. The presence of copper or arsenic in the iron will, of course, have a tendency to hold sulphur in the residue as their sulphides are not decomposed by HCl. Phillips has shown that the sulphur retained by the residue is frequently in the form of difficultly volatile organic compounds and may be distilled off by prolonged boiling of the solution.

The H_2S evolved is very easily decomposed by comparatively feeble oxidizing agents, water being formed and free sulphur deposited. *Prolonged* contact with air and sunlight, the presence of $FeCl_3$, traces of chlorine, all act on it in this way, and must be avoided in the process. There is no necessity, however, of working in an atmosphere of H or of CO_2 if the process is *rapidly conducted.* On the other hand, slow evolution, or the use of HCl containing

traces of Cl or Fe Cl_3 will cause decomposition of the H_2S and retention of sulphur in the residue.

Rusting of the drillings previous to the addition of HCl leads to the formation of $FeCl_3$ and may cause a separation of sulphur from the gas in the flask. Dilute HCl (1:1) is usually used in these methods but according to the writer's experience this sometimes fails to cause complete evolution of the S as H_2S, where the concentrated acid succeeds. See Phillips. Jour. Am. Chem. Soc., 1895, p. 891.

The sulphur in the evolved gas may be estimated gravimetrically after absorbing it in an oxidizing liquid, such as bromine water and HCl, a dilute solution of potassium permanganate, or peroxide of hydrogen, which will convert it into SO_3. It can also be absorbed in a solution of some metallic salt such as alkaline lead acetate, silver nitrate or alkaline cadmium chloride. In this case the precipitated metallic sulphides are separated and the sulphur in them oxidized and determined as $BaSO_4$. While the H_2S is easily absorbed the organic sulphur compounds are only slowly and incompletely taken up. Long boiling is frequently necessary to drive them completely out of the flask in which the iron is dissolved. It is evident from what has gone before that none of the forms of the evolution method can be relied upon to give the total sulphur in irons which give off these organic sulphur compounds. Some sulphur will be left in the flask unless the boiling is greatly prolonged and some will escape even powerfully oxidizing absorbents.

DROWN'S METHOD WITH POTASSIUM PERMANGANATE.

This is the least troublesome of the gravimetric evolution methods. It is accurate for those metals which evolve their sulphur as H_2S. The H_2S is absorbed by an alkaline solution of $KMnO_4$. This is a more energetic absorbent than the neutral solution originally proposed by Dr. Drown, hence the gas can be sent through the liquid much more rapidly without danger of any S escaping absorption.

As the rubber corks and tubes used in the apparatus contain sulphur they must be kept from contact with the absorbing solution. They should be prepared for use by first boiling them for some time in a dilute solution of NaOH, then rubbing them well to remove any crust from the surface, and finally washing them thoroughly with water and dilute HCl.

Apparatus.—This is shown in fig. 3 and consists of a flask F of 500 c.c. capacity and fitted with a rubber stopper, a glass funnel tube G provided with a stop cock, and a delivery tube H, in which are blown two or three good sized
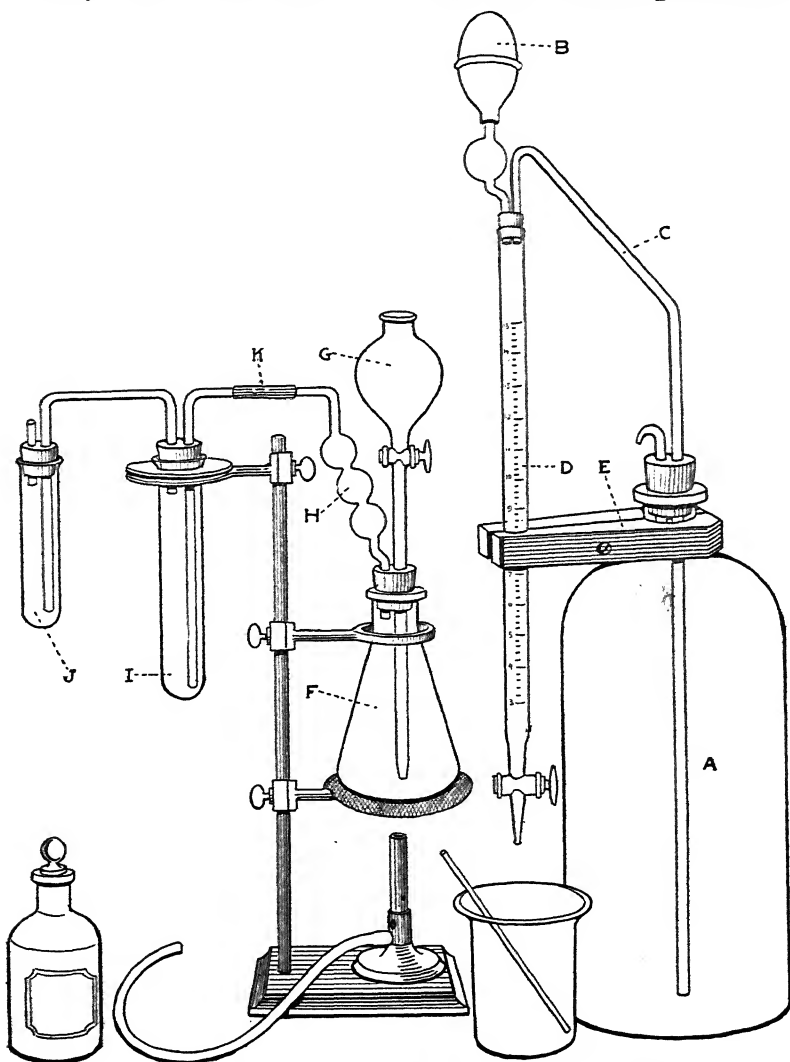
FIG. 3.—Apparatus for the determination of sulphur by evolution.

bulbs. These bulbs serve to arrest the liquid condensing in the tube and allow it to return to the flask instead of working over into the absorption tubes. The delivery tube should carry the gas down to the bottom of a large test tube I, eight inches deep and one inch and a quarter wide and fitted with a rubber stopper through which a second tube carries the gas into a second smaller test tube J, which serves to catch any absorbable sulphur compounds escaping the first test tube. This guard tube will rarely show any sulphur. (The bottle, A, holds the iodine solution for the volumetric process, which can be drawn over into the burette, D, by working the rubber bulb, B. This has a small hole in the top which can be covered by the finger and act as a valve, thus allowing the liquid to be "pumped" over into the burette. The small bulb is filled with cotton to prevent anything working down into the burette from the bulb.)

Process.—Weigh 5 or 10 grams of the drillings, according to the percentage of sulphur contained in the metal, into the flask. Put into the first test tube in the absorbing train 30 c.c. of a solution of potassium permanganate, 5 grams to the litre, and 30 c.c. of a ten per cent. solution of pure sodium hydroxide. Charge the second tube in the same way, using half the amounts. Add water to the tubes until they are about half filled by the liquid; there should be a space of three or four inches above the liquid in each tube. Now connect up the apparatus, put 50 or 60 c.c. of concentrated HCl into the funnel tube, and cautiously run this into the flask. This should be done rapidly but not so as to cause such an evolution of gas as to form very large bubbles in the tubes, or to throw the absorbing liquid up against the corks. As the absorbing liquid is alkaline, the evolution of the gas can be quite rapid without danger of H_2S escaping absorption, and the more rapidly the iron is dissolved the larger the percentage of the sulphur which appears to be evolved in an absorbable form. When the action becomes slow and the iron is nearly all dissolved, bring the contents

of the flask to boiling and boil until the liquid in the first tube grows quite warm and MnO_2 begins to separate. The steam will drive over all the H_2S and also to some extent carry over difficultly volatile sulphur compounds, leaving the residue in many cases practically free from sulphur. Now remove the lamp, being careful to immediately open the stopcock of the funnel tube so as to admit air to the flask as it cools, or a vacuum may form and the contents of the test tubes be drawn back into the flask.

Disconnect the test tubes, empty them into separate beakers, washing out both the connecting tube and the test tubes with water. Any MnO_2 adhering to the tubes should be dissolved off with a little HCl, and the solution added to the liquid from the test tubes. A little oxalic acid should be added to the HCl so used. The contents of the second tube should be alkaline at the end of the process though the HCl distilling over will probably have neutralized the alkali in the first tube and dissolved most of the MnO_2. Now heat the contents of the beakers, and if not already acid add a slight excess of HCl which may cause MnO_2 to separate. Drop in a solution of oxalic acid carefully until the MnO_2 is all dissolved and the solutions are colorless. Add to each beaker 15 c.c. of a ten per cent. solution of $BaCl_2$, settle, filter, wash and weigh the $BaSO_4$ as usual. The liquid from the second tube should show no more than a trace of $BaSO_4$. Filter this in with the first precipitate. Should the second tube show much precipitate repeat the process, evolving the gas more slowly. Run a careful blank on the permanganate, soda, acids, etc., using the same amount of each as is taken in the analysis, and deduct the weight of the $BaSO_4$ found in this (due to impurity of reagents) from that found in the analysis.

Instead of using concentrated HCl in the process, many prefer to use the acid diluted with its own volume of water. It is easier to conduct the process in this way, as less of the acid distills over into the tubes, but it is a little more liable to leave sulphur behind in the residue.

Aspiration of air or CO_2 through the flask to remove the last traces of H_2S is entirely unnecessary with the small percentages of sulphur found in iron and steel.

Examination of the Residue in the Flask for Sulphur.—Filter the contents of the flask through a 9 cm. filter, wash the residue thoroughly and dry it at a temperature not exceeding 100° C. Open out the filter and brush the residue into a small beaker. Add 10 c.c. of concentrated HNO_3 and a small crystal of $KClO_3$. Boil down to dryness, take up by heating with 5 c.c. of concentrated HCl, dilute to 30 or 40 c.c., filter and add 5 c.c. of $BaCl_2$ solution to the filtrate. Let stand till any precipitate of $BaSO_4$ settles, filter it off and weigh it.

The residue may also be treated by fusion exactly as an iron ore, of course using smaller quantities of fluxes.

Drown—Trans. Am. Inst. Min. Engs., Vol. II, p. 224.

Auchy—Jour. Am. Chem. Soc. 1896, p. 404.

For the use of other absorbents, see Trans. Am. Inst. Min. Engs., Vol. X. p. 187. (Cadmium). and XII, p. 507. Bromine). Chemical News, XLVI, p. 199. (Peroxide of Hydrogen.) For the use of lead salts, see Fresenius Quantitative Analysis.

THE IODINE METHOD.

DETERMINATION OF THE H_2S BY TITRATION WITH IODINE.

This is the most generally used of the evolution methods, and is extremely rapid. Its results will be lower than those given by the direct oxidation methods with all metals containing considerable combined carbon, but as the results are concordant, they serve for furnace control. All sulphur not evolved as H_2S is necessarily lost in this process. Hence concentrated acid will in many cases give higher results than the dilute acid generally used. The H_2S evolved on dissolving the iron is absorbed in an alkaline liquid, either NaOH, KOH, or an ammoniacal solution of cadmium or of zinc. An advantage in the use of the two latter lies in the fact that the H_2S is fixed in a visible form (CdS or ZnS), and one which is not so subject to alteration on standing as are the alkaline sulphides. Further, the KOH and NaOH are very liable to contain oxidizing impurities such as nitrites or ferric hydroxide which liberate iodine from KI, and thus will cause false results in the titration. These impurities would not be discoverable in an ordinary blank, but such a solution would give a blue color with starch immediately if acidified and tested by a few drops of a solution of KI alone.

The reaction between H_2S and a strongly ammoniacal solution of cadmium chloride is as follows:

$$H_2S + CdCl_2 + 2\,NH_4OH = CdS + 2\,H_2O + 2\,NH_4Cl.$$
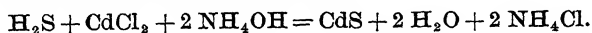
If the liquid containing the precipitate of CdS is diluted with a large volume of water and a sufficient excess of HCl added, H_2S is

again liberated by the following reaction:

$CdS + 2\,HCl = H_2S + CdCl_2.$
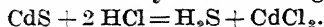
A considerable excess of HCl is required to cause the complete disappearance of the yellow precipitate.

The presence of a *large volume* of cold water is necessary so that the H_2S shall not escape, but will remain in solution in the water. This solution of H_2S is then titrated by a standard solution of iodine. The iodine unites with the hydrogen, setting free the sulphur:

$H_2S + 2\,I = 2\,HI + S.$
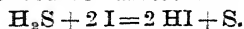
A little solution of starch is added to the liquid, and the least excess of iodine is shown by an intense blue color ("iodide of starch").

The liberated sulphur causes the liquid to become curiously opalescent and show various colors, but this does not at all obscure the "end reaction," which is very sharp.

The solutions needed are standard iodine and starch.

Preparation of the Starch Solution. — Stir 5 grams of starch into 200 c.c. of cold water. Heat the liquid to boiling with constant stirring until the starch is thoroughly dissolved. Now dilute the liquid with cold water to about a litre, and add 10 grams of crystallized $ZnCl_2$. Let the solution settle for some time, and pour off for use the nearly clear supernatant liquid. This solution is very sensitive and keeps indefinitely.

A solution of one gram of starch in 200 of boiling water alone may be used, but it must be made fresh every day.

Preparation of the Iodine Solution. — Weigh on a watch glass 3.956 grams of pure resublimed iodine. Put it into a small beaker, add about six grams of pure potassium iodide (free from iodate) and 10 c.c. of water. Let stand in the cold until all the iodine dissolves. Then transfer to a graduated flask and dilute to one litre.

One cubic centimeter of this solution should be equivalent to 0.0005 gram of sulphur. If five grams of metal are taken for the analysis each c.c. of iodine solution consumed will be equivalent to 0.01 per cent. of sulphur.

In the reaction $H_2S + 2\,I = 2\,HI + S$, two atoms of I are equivalent to one atom of S, or 253.7 by weight of $I = 32.06$ of S. To find the amount of I, which must be contained in 1 c.c. to give a solution of

the above value in sulphur, make the proportion .0005 : x = 32.06 : 253.7. This gives x = .003957, which amount in 1 c.c. will be 3.957 grams per litre.

Iodine is insoluble in water, but is easily and rapidly dissolved in *a very concentrated* solution of KI, though very slowly in a dilute one.

The iodine solution is not constant; hence, its strength must be determined frequently.

Standardizing the Iodine Solution.—Prepare the following solutions:

A. 8 grams crystallized sodium thiosulphate dissolved in water and diluted to one litre.

B. 0.1531 gram of fused potassium bichromate is dissolved in water and diluted to 100 c.c. If more convenient this solution may be made by diluting 10 c.c. of the bichromate solution used in the iron assay (of which 1 c.c. equals 0.01 Fe) to 57.1 c.c. 10 c.c. of this solution will liberate iodine from KI equivalent to .005 sulphur.

Measure with a pipette 10 c.c. of the thiosulphate solution A into a beaker. Add 100 c.c. of water and 1 c.c. of starch solution. Now run in the iodine solution from a burette until the last drop gives a decided blue color not disappearing on stirring. Note exactly the amount used. Repeat the determination two or three times, (the results should agree almost exactly,) and take the average as the amount of iodine solution equivalent to 10 c.c. of the thiosulphate.

Measure 10 c.c. of the bichromate solution B into a beaker. Add 50 c.c. of cold water and then about 0.5 gram of pure KI. When the KI is dissolved add 5 c.c. of concentrated HCl.

The KI must be free from iodate. It may be tested by dissolving a portion in water, adding some starch solution and a little HCl. The liquid should not show more than a trace of blue color and should become absolutely colorless on the addition of a small drop of the thiosulphate solution. The acid used must be free from chlorine or ferric chloride. When diluted it should give no blue color on the addition of KI and starch.

Let the mixture stand six or seven minutes without warming (which would volatilize iodine). Dilute to 100 c.c. and add 10 c.c. of solution A and 1 c.c. of starch solution. Should this color the liquid blue, add 10 c.c. more of the thiosulphate solution which will make it colorless. The first 10 c.c. is usually sufficient. Now *immediately* titrate the excess of thiosulphate with the iodine solution, adding it till the blue color is developed. Note exactly the volume of the solution used; call it R.

It is important that there be no delay between the addition of the solution "A" and the iodine titration on account of the presence of free HCl in the liquid. Thiosulphate is slowly decomposed by HCl with the separation of sulphur and the formation of H_2SO_3 which absorbs twice as much iodine.

By keeping the excess of thiosulphate small and titrating it within one minute, correct results can be obtained.

Now the difference between "R" and the number of c.c. of the iodine solution that are equivalent to the number of c.c. of the thiosulphate solution "A" added to the bichromate and iodide as above, is the volume of the iodine solution that is equivalent to 0.005 gram sulphur, and 0.005 divided by this difference is the value in sulphur of 1 c.c. of the iodine solution. This is the factor by which to multiply the number of c.c. taken in the analysis in order to obtain the amount of sulphur present.

Example: Suppose 10 c.c. of solution "A" equals 10.6 c.c. iodine solution. Second, that 20 c.c. of "A" were added to the 10 c.c. of "B" and the KI, and that the mixture required 9.8 c.c. of iodine solution on the titration back; that is, "R" equals 9.8. As the 20 c.c. of "A" alone would equal 21.2 c.c. of iodine, we have $21.2 - 9.8 = 11.4$, which is the number of c.c. of iodine solution equivalent to 0.005 of sulphur. Because this is the sulphur equivalent to the iodine that is liberated from the KI by the bichromate. Further, 0.005 divided by 11.4 equals 0.000439, which is the amount of sulphur to which 1 c.c. of the iodine solution is equivalent.

The reactions upon which this process of standardizing depend are:

1. $2 Na_2S_2O_3 \, 5 H_2O + 2 I = 2 NaI + Na_2S_4O_6 + 5 H_2O.$ (The crystallized thiosulphate contains 5 molecules of water.)

2. $K_2Cr_2O_7 + 6 KI + 14 HCl = 8 KCl + 2 Cr Cl_3 + 7 H_2O + 6 I.$

Two molecules of thiosulphate weigh 496.64, and as 2 molecules of thiosulphate are equivalent to 2 atoms of iodine (253.7) we have the proportion $496.64 : 253.7 = 7.75 : 3.957$, 7.75 being the amount of thiosulphate which should be dissolved in 1 litre to give a solution equivalent to the iodine, but as it is desirable that this solution be a a little stronger, 8 grams are actually taken.

The thiosulphate solution is not constant, hence cannot be used as an absolute check on the iodine solution, but only as a means of comparing it with an absolutely known amount of iodine. This definite amount of iodine is obtained from the action of bichromate on an excess of KI in the presence of HCl. The reaction between KI and $K_2Cr_2O_7$ is not instantaneous, but rapidly becomes complete.

The relation between the $K_2Cr_2O_7$ and the I is $294.5 : 761.1$, hence $0.01531 \ K_2Cr_2O_7$ will liberate 0.03957 gram of iodine, the amount which should be present in 10 c.c. of the iodine solution if its strength were exactly right.

The operation itself consists therefore in finding how much of the iodine solution to be standardized, is required to titrate the amount of the thiosulphate solution which is equivalent to exactly 0.03957 gram of iodine, as liberated by the bichromate. Thus we find *first* how much of the iodine solution is equal to a certain amount of the thiosulphate solution; *second*, how much of the same iodine solution is equal to what is left after the same amount of thiosulphate has been acted upon by 0.03957 gram of iodine, and the difference is obviously the amount of iodine solution which contains 0.03957 gram of iodine, that is to say will be equivalent to 0.005 of S; but this should be 10 c.c., hence the difference between 10 and the amount taken is the amount the solution is off the standard.

The only precautions to be noted are the necessity of giving *time* for the $K_2Cr_2O_7$ to react on the KI and the necessity of avoiding *heat* as iodine is readily volatilized from this solution.

The HCl used must be free from all impurities which liberate iodine from KI (Cl, $FeCl_3$, $CuCl_2$, etc.).

The iodine solution may also be standardized against a sample of iron or steel similar to that to be analyzed in which the sulphur has been accurately and repeatedly determined by the direct oxidation or nitric acid method.

Treat a given weight of the metal by the regular process and determine the volume of the iodine solution required to titrate the

H_2S evolved Then from the known sulphur percentage in the metal calculate the sulphur value of 1 c.c.

Make a factor of correction to apply to the iodine solution. This method of standardizing has the advantage of causing all errors of solution. evolution and oxidation to affect the standard and sample alike, and makes the evolution method give results comparable with the gravimetric method. It should always be used where a material of generally uniform character has to be tested as manufactured. As the heat treatment and the nature of the metal cause differences in the percentage of sulphur evolved as H_2S. an iodine solution standardized on metal should never be used for a metal made by a different process. as for example. one standardized on pig iron for steel. See Wilson. Jour. An. and App. Chem.. Vol. V, p. 439.

Cadmium Solution.—Dissolve 4 grams of cadmium chloride in 100 c.c. of water, and when dissolved add an equal volume of strong ammonia.

Apparatus.—This consists of a 500 c.c. flask, funnel tube and delivery tube similar to that used in the Drown method. (See Fig. 3.) The delivery tube should extend to the bottom of the large test tube which should be $1\frac{1}{4}$ to $1\frac{1}{2}$ inches in diameter and 8 inches deep. Only a single receiving tube is necessary in this process, there being no danger of H_2S passing through unabsorbed even with a very rapid evolution of the gas. In place of the test tube some use a large flask, diluting the absorbing liquid correspondingly. The titration may then be made in the same flask without transferring the liquid.

Amount of Metal Taken.—This may be 5 grams for ordinary irons or 10 grams if the sulphur is very low. If the iodine solution is a little "off the standard;" that is, if 10 c.c. are equal to a little more or less than 0.005 sulphur; it is more convenient, instead of correcting each reading by multiplying it by the true sulphur value, to change the amount of the sample taken so that 1 c.c. of the iodine solution shall represent .01 per cent. of sulphur.

For example: Suppose that the iodine solution is too weak and that 1 c.c. is only equal to .0004854 gram of sul-

phur instead of .0005 gram. In this case weigh out 4.854 grams of the metal for the determination. Then obviously each c.c. of the iodine solution used in the titration will stand for .01 per cent. of sulphur, and the calculations which would be necessary if 5 grams had been taken will be avoided.

The foregoing method of applying the correction factor of a volumetric solution to the amount weighed out may be applied to any similar process; as, for example, in the determination of iron, phosphorus or manganese; and where many analyses are to be made will save much time as well as diminish the chances of error involved in the calculations.

PROCESS FOR THE ANALYSIS.

Transfer the weighed metal to the flask. Pour 5 c. c. of cadmium solution into the absorbing test tube and add to it 10 to 15 c.c. of strong NH_4OH. Now fill the tube with water to a depth of at least six inches.

Put 50 c.c. of concentrated HCl into the bulb of the funnel tube; then run it into the flask rapidly. But avoid so rapid an evolution of gas as to throw the liquid out of the tube or to make bubbles large enough to fill the tube. When the evolution of gas slows up, shake the flask containing the iron and then gradually heat it to boiling. Boil the solution gently until the iron is dissolved and very little gas continues to pass through the liquid in the tube. The solution in the tube must be kept alkaline by adding more NH_4OH if necessary. The CdS separates as a yellow flocculent precipitate.

When using concentrated HCl a considerable amount of acid distills over, but by using sufficient ammonia it will do no harm. After the iron is all dissolved and but little more gas is coming over, remove the lamp and open the stopcock in the funnel tube. Now detach the delivery tube and empty the test tube into a large beaker or dish. Add 300 or 400 c.c. of cold water, and then enough HCl to dissolve the precipi-

tated CdS. Now add 1 c.c. of the starch solution and titrate with the iodine solution, adding it until the last drop changes the opalescent liquid to a deep blue not disappearing on standing two or three minutes.

The number of c.cs. used, after correction for standard, will give the amount of sulphur in hundredths of a percent. Always make a blank test on the reagents; they will usually consume a little iodine which must be deducted from that used in the analysis.

Additional Notes on the Process.—Use pure gum rubber tubing in the connections. White or red rubber may contain metallic sulphides evolving H_2S when acted upon by the HCl vapor, thus causing errors.

It is essential that the process be carried through promptly. There should be no delay in titrating. If the solution containing the CdS be allowed to stand it may lose H_2S or the sulphides may oxidize. This is especially important after the addition of the HCl, as the free H_2S will oxidize very rapidly on standing. Zinc salts (acetate or sulphate) may be used in the place of cadmium with satisfactory results.

The Use of NaOH instead of $CdCl_2$.—The process is conducted as before, except that the absorption tube is filled with 80 c.c. of a fifteen per cent. solution of NaOH. After the evolution of the gas, wash out the tube into a large beaker, dilute as before with cold water, acidify, add starch solution and titrate. Most caustic soda contains a little iron as ferric hydroxide, which dissolves in the concentrated solution but separates on dilution; hence, the 15 per cent. soda solution should be prepared some time before use, and the clear liquid decanted from the precipitate which usually settles. Test the solution also for nitrites and hypochlorites by acidifying a portion with HCl, and then adding KI and starch paste. It must show no blue color. In acidifying the soda solution before titration add a drop of phenolphthalein solution, and then add the HCl till the red color is discharged. The HCl must be pure. It will occasionally contain traces of SO_2 which would of course vitiate the results.

The cadmium method is sometimes modified by filtering off the CdS and putting the filter and precipitate into a large volume of water, adding HCl and titrating. This avoids the presence of a large

amount of ammonium salts and of any hydrocarbons absorbed in the liquid. It has been claimed that these act slightly on the iodine. The advantage of this modification is very slight if any, as the evolution process usually gives low results any way.

THE DETERMINATION OF CARBON IN PIG IRON AND STEEL.

The carbon in gray pig iron mostly occurs as " free carbon " or graphite. A portion is, however, combined with the iron, forming a carbide and constituting the so-called "combined carbon."

In white iron and "chilled iron," as well as in steel, especially " mild " or low carbon steel, most of the carbon is combined.

Ferrosilicon contains practically no combined carbon. The carbon in " Malleable Iron " (made by the prolonged annealing of white iron), contains carbon in an amorphous form, different from graphite, but not in combination with the iron. When these metals are dissolved in hot HCl the graphite or free carbon is left undissolved as a black scaly or spongy residue: while the combined carbon, uniting with the hydrogen, forms hydrocarbons part of which remain in the liquid and residue and part of which pass off in the gas. The uncombined carbon is also left in the residue if the metal is dissolved in HNO_3 sp. gr. 1.2, none of it being oxidized by the acid. In this case, the combined carbon all passes into solution, forming a highly colored compound which gives a more or less intense brown tint to the liquid.

Carbon is usually determined after oxidizing it to CO_2, the gas being absorbed in a weighed amount of KOH, or other absorbent. The gas may also be determined by measuring its volume by the processes of gas analysis.

Journal Soc. Chem. Ind., 9, p. 768; 10, p. 658; also p. 1033.

It can also be determined by absorbing it in a solution of $Ba(OH)_2$ and filtering off and weighing the $BaCO_3$ formed. For details see " Methods of Iron Analysis," F. C. Phillips.

The carbon is converted to CO_2 when iron is completely burned in oxygen gas. Unfortunately this simple method cannot be used in most cases, because when iron fragments are heated in oxygen they become coated with a layer of oxide, which protects the interior from the further action of the gas, and so a portion of the carbon remains unburned, even hours of heating failing to reach it all.

Hence, this method is only applicable where the iron can be reduced to a *very fine powder*, a condition unattainable in practice with many irons.

Usually the first step in the determination of carbon is to liberate it from the iron, by dissolving the latter in some solvent which will not act on the carbon but will leave it all unattacked in the residue.

which will not act on the carbon but will leave it all unattacked in the residue.

The carbon thus liberated is filtered out on to ignited asbestos and then burned to CO_2, in oxygen or by heating with chromic acid and sulphuric acid.

Several solvents have been used. The essential condition is that no hydrogen gas be liberated, as it will form hydrocarbons and carry off carbon, and that no strong oxidizing agent be present, which will oxidize carbon.

The most rapid solvent for iron which fulfills these conditions is a saturated solution of potassium or ammonium cupric chloride.

The reaction by which the iron is dissolved is

$$Fe + 2 (K_2 Cu Cl_4) = Fe Cl_2 + Cu_2 Cl_2 + 4K Cl..$$
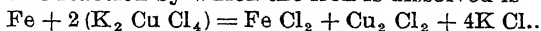
The K Cl serves to hold the cuprous salt in solution and greatly hastens the action.

This solution has a tendency to dissolve organic matter, which is liable to be subsequently precipitated with the carbon in the steel. This is especially true of the ammonium salt. It being very difficult to obtain it free from organic matter, (derived from the ammonium salts used in its manufacture.) The salt should be thoroughly purified by re-crystallization. The potassium salt is more easily obtained free from this contamination and for this reason is to be preferred.

A large excess of the solution is required to prevent separation of metallic copper with the carbon.

The carbon residue retains chlorides very difficult to wash out, and which cause trouble in the subsequent combustion. If any metallic copper is precipitated and left mixed with the carbon, it will form basic subchlorides nearly insoluble in water. The spongy carbon is best freed from chlorides by treatment with dilute HCl and then washing thoroughly with water.

Instead of using a neutral solution of potassium cupric chloride, it is usually acidified with a little HCl. The presence of this acid will cause no loss of carbon, provided the solution is kept cool while the iron is dissolving.

The solution after having been used can be regenerated and used again by passing chlorine gas through it until the Cu_2Cl_2 is changed back again to $CuCl_2$.

Sargent, Journal American Chem. Soc. 1900. Page 210.

For important papers on the carbon determination consult—

Trans. Am. Inst. Min. Engs., vol. XIX, p. 614.
Jour. An. and App. Chem., vol. V, p. 129.
Jour. An. and App. Chem., vol. V, p. 122.
Journal Am. Chem. Soc., 1893, Page 443 and 526; 1895, Page 873; 1898, Page 243.

Process—Solution of the Metal and Separation of the Carbon.
Prepare a solution of the double chloride of copper and ammonium or potassium. Use the purest crystallized salt obtainable. Dissolve one part in three parts of pure water, free from grease or organic matter, adding about 5 per cent. of concentrated HCl. Let the liquid settle, decant off the *clear* solution, and filter any turbid portion through ignited asbestos.

Weigh out 2 grams of pig iron, 3 grams of high carbon steel or 5 grams of low carbon steel or wrought iron. Put this metal into a 200 or 250 c.c. beaker, and add at once the copper solution, using 50 c.c. for each gram of the sample taken. Stir the liquid continuously until the iron is dissolved.

If an air blast is available, this stirring can be accomplished by blowing air through the liquid. The air should be first passed through a tube filled with absorbent cotton to filter out any dust.

The completion of the reaction is recognized by the residue becoming light and "flotant." At first more or less copper will separate, but continued stirring will bring it into solution.

As soon as all the separated copper has disappeared, let settle a few minutes if necessary and decant onto an asbestos filter, disturbing the carbon as little as possible. Add 10 c.c. of dilute HCl (1:1), washing down the sides of the beaker with this acid. Decant this through the filter. When the liquid has all run through wash out the beaker and transfer all adhering carbon to the filter with the dilute HCl.

Wash the carbon on the filter twice with acid. Let the acid run through slowly to give it time to act. Now wash with water until all the HCl is removed and the filtrate does not react with Ag NO$_3$.

The filtrate will be dark colored at first, but when diluted with the HCl and water will become lighter, and

then must be carefully examined to see that no particles of carbon have run through the filter.

The drillings of metal must be free from all *grease* or intermixed particles of wood, straw or paper. They may be separated from the latter by a magnet, and from the former by washing them with pure ether, and drying. Care in drilling and handling the sample will render this treatment unnecessary.

The "weighing out" of pig iron for this carbon determination is a matter of great difficulty, as the fine, dusty portion is usually higher in carbon than the lumps. A method proposed by Dr. Shimer is to moisten the drillings with alcohol, so that the fine may stick to the coarse. Then take a portion of approximately the right weight, put it on a weighed watch glass, dry it carefully and re-weigh. Use this amount in the determination.

Preparation of the Asbestos Filter.—The form of filter shown in Figure 4, is a slight modification of one described by Professor Arnold in his "Steel Works Analysis" It will be found very convenient. A is an ordinary heavy glass filtering flask such as is used with the Bunsen Filter Pump. It should have a capacity of about 500 c.c. B is a piece of glass tube with a uniform bore of about ⅝ of an inch and about 9 inches long. This passes through the rubber stopper in the neck of the flask. The hole in this stopper can be drilled with a large cork borer moistened with a dilute solution of KOH. Into this tube a second tube C is inserted. This is of such a size as to just slip freely through the larger tube. It should be about one inch longer than the first tube and have the ends ground off square. The apparatus should be so arranged that when the smaller tube rests on the bottom of the flask it will leave about two-thirds of the upper tube unoccupied. Now cut a disc of platinum
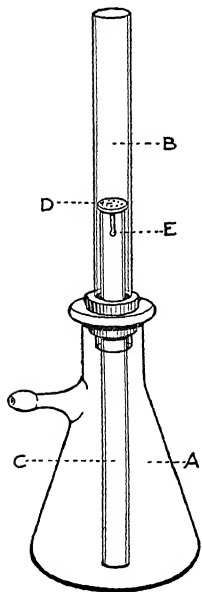
FIG. 4.
CARBON FILTER.

foil of such a size that it will freely slip into the larger bent and rest in place on the end of the inner tube. This platinum disc should be punched full of holes with a needle. It is advantageous to solder (with a bit of gold and a blow pipe), a piece of stiff platinum wire, E, to the center of this disc which will stick down into the lower tube and keep the disc in place. This wire will also serve as a convenient handle for lifting the platinum from the asbestos matt after it is removed from the tube.

Prepare the asbestos for the felt as follows: Select long fibered asbestos. (Not the "cottony" kind, but that with rather stiff fibers). Cut it across the fibre into pieces $\frac{3}{16}$ of an inch long. Ignite these in a platinum crucible at a low red heat for at least thirty minutes. When cool transfer them to a clean porcelain mortar and "macerate" them to a pulp with strong HCl. Now dilute the paste with a large amount of water, pour into a beaker and allow the mixture to settle until the fibrous mass collects at the bottom, leaving the fine, milky silt still in suspension. Decant from the fibers and repeat the washing until the wash water comes off only slightly milky. Asbestos prepared in this manner makes a felt that filters very rapidly. If the fine slimy material that is formed during the felting is left in the mixture it will clog the filter and make it work badly. Preserve the felt in water in a stoppered bottle. To form the filter pour enough of the suspended felt into the tube to form a layer about $\frac{1}{16}$ of an inch thick when drawn down by suction on to the platinum disc in the tube, then attach the suction pump. Exactly the right amount must be learned by experience. But when right it will filter rapidly and yet retain the finest carbon.

Draw a little water through the felt to wash it before pouring on the carbon solution. After the carbon is filtered and washed take the stopper with the tubes out of the bottle, wash off the smaller tube and then push it carefully through

the larger tube, forcing out from below the disc carrying the felt and carbon. The felt and carbon can now be dropped into the combustion flask or into a platinum boat for combustion in oxygen. With a little care no carbon whatever will be left adhering to the tube. Should a little adhere it can be washed off into the flask with a few drops of water or wiped off with a small tuft of ignited asbestos.

DETERMINATION OF THE CARBON BY OXIDATION WITH CHROMIC ACID AND WEIGHING THE CO_2 PRODUCED.

Carbon in any form is rapidly and completely oxidized to CO_2 when heated with chromic acid and an excess of sulphuric acid.

It is essential that the sulphuric acid be sufficiently concentrated; if too dilute, the oxidation will be incomplete and some CO will be formed which will escape the absorption apparatus. The strength of acid necessary depends somewhat on the condition of the carbon, as the amorphous carbon from steels is more easily oxidized than the graphite from pig iron. In no case should the mixture contain less than 70 per cent of H_2SO_4 while for pig irons enough should be present to give, on boiling, a trace of white fumes of H_2SO_4. If not present in large amount these white fumes will be arrested in the purifying train. They represent only a very minute quantity by weight. When the acid is of this strength the mixture will give off some oxygen gas on boiling.

If the carbon retains chlorine or chlorides, chlorine and chlorochromic acid gas may form, escape with the CO_2 and be absorbed by the KOH, vitiating the results unless special means be provided for absorbing them in the purifying train.

The H_2SO_4 used must be purified from all organic matter.

Arrangement of the apparatus.—Fig. 5 shows a convenient form of train for the use of students. It is compact, needs no special clamps, and can be taken apart and set away in a laboratory desk. C is an Erlenmyer flask of about 250c.c. capacity, fitted with a 2-hole rubber stopper; into one hole is inserted a bulb funnel tube B, having a glass stopcock, and into the other a delivery tube M, for the gas.

This latter should be of rather large diameter and so inclined that everything condensing in it will run back into the flask. It is a good plan to have it cooled by a "water jacket" D, consisting of a
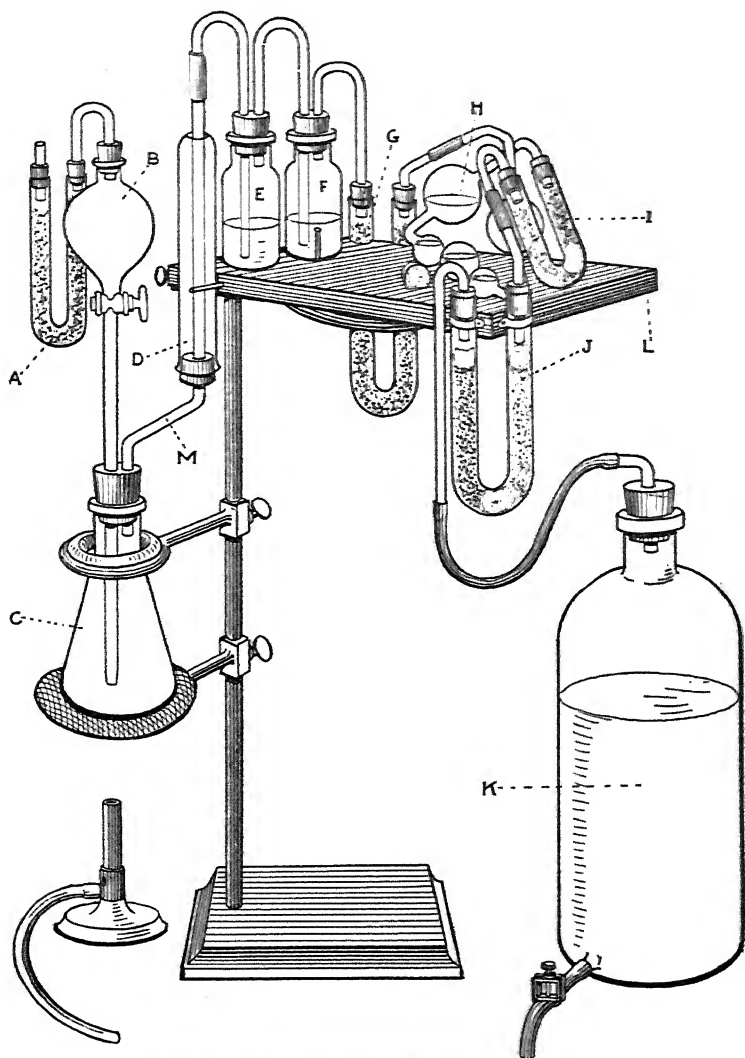
FIG. 5.—Carbon Train for chromic acid method.

larger tube surrounding the smaller, the space between the two being filled with water.

A small "guard tube" A, filled with "soda lime" is fitted to the top of the funnel tube.

This serves to remove any CO_2 from the air drawn into the flask. It must be arranged so as to be easily connected and disconnected.

The delivery tube is connected with the purifying and absorbing apparatus (or "train") arranged in the order shown.

"E" Fig. 5 is a bottle of 50 or 75 c.c. capacity, containing about 30 c.c. of a solution of silver arsenite in dilute sulphuric acid.

This serves to absorb any HCl, Cl, or CrO_2Cl_2 in the gas. A solution of silver sulphate may be used instead, but this does not absorb chlorine nor chloro chromic acid and is usually preceded by a bottle containing pyrogallic acid dissolved in a solution of potassium oxalate (Langley). When using the arsenite this is unnecessary, as it is oxidized to arsenate by the chlorine and the silver precipitated as chloride.
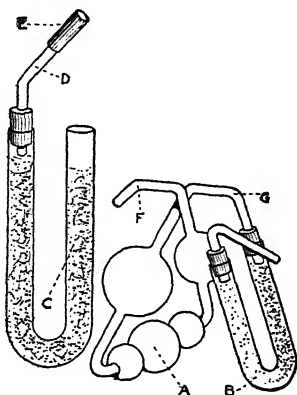
FIG. 6.

The arsenite solution is prepared as follows: Dissolve 2 grams of pulverized As_2O_3 in the smallest possible quantity of a dilute solution of KOH. Dilute to 250 c.c. and add dilute H_2SO_4 till the solution is neutral to litmus paper. Now add a solution of $AgNO_3$ as long as a yellow precipitate forms, carefully keeping the solution neutral by adding a solution of KOH drop by drop as needed. Stir the liquid till the precipitate clots and let it settle, and wash it thoroughly by decantation. Finally dissolve the precipitate in a slight excess of dilute H_2SO_4. (10 per cent.) Dilute to about 150 c.c. and filter from any undissolved AgCl. The solution keeps well.

The silver sulphate is made by dissolving about 0.5 gram of $AgNO_3$ in a little water adding 1 c.c. concentrated H_2SO_4, evaporating till the

HNO_3 is all expelled, cooling and diluting largely with water. Ag_2SO_4 is only sparingly soluble.

" F " is a bottle containing 20 or 30 c.c. of pure concentrated H_2SO_4.

This takes out all the water vapor from the gas.

"G" is a U-tube containing granular $CaCl_2$. Fill about an inch of the tube, on the side next to the H_2SO_4 with cotton and moisten the top of this with a drop of water. (Blair). It is shown with its connecting tube in Figure 6 "C."

The object of this $CaCl_2$ is to absorb H_2O and to bring the gas stream entering the absorption apparatus (H and I) into the same condition as to moisture, in which it leaves it. H_2SO_4 will dry air more completely than $CaCl_2$, hence if the gas entered through H_2SO_4 and left through $CaCl_2$ it would carry out more moisture from the KOH bulbs than it brought in and so result in loss of weight. It also serves to catch any white fumes of H_2SO_4 carried over by the gas.

Dried $CaCl_2$ and not the fused salt should be used, This latter is usually alkaline from free CaO and will absorb some CO_2.

" H " (Fig. 5) shows the Liebig's potash bulbs. These contain a clear solution of KOH of about sp. gr. 1.27, (about 30 per cent.)

This solution absorbs the CO_2, but not *completely* unless the gas stream is slow. The solution gives up a little water to the gas passing through. If made stronger than directed it deposits K_2CO_3 which may clog up the tube.

As caustic potash frequently contains nitrites and almost invariably traces of $Fe(OH)_2$, a fresh solution will absorb oxygen, the $Fe(OH)_2$ gradually precipitating as $Fe(OH)_3$. If the potash bulbs are filled with such a solution they will frequently continue to increase in weight for some time if air alone is aspirated through them. This troublesome difficulty may be entirely overcome if the potash solution is heated to boiling before using, and a solution of potassium permanganate added drop by drop until a faint persistent green tint is produced. The liquid is then allowed to cool and settle, and the clear solution decanted for use.

"I" is a small U-tube, with the limb next the potash bulbs filled with granular soda lime. This should not be too dry. The other limb is filled with granular $CaCl_2$.

This tube serves to catch the trace of CO_2 escaping the bulbs, and also to retain the moisture carried over from the potash bulbs. Soda lime is a more rapid and complete absorbent for CO_2 than the KOH in the bulbs, but it is soon exhausted. By letting the bulbs do most of the work and only using the soda lime as a guard, it lasts for several operations and retains every trace of the CO_2. The potash bulbs and the soda lime+$CaCl_2$ tube, are the parts of the train to be *weighed*. They may be weighed separately or together. In the latter case they should be permanently combined into one piece as shown in fig. 6, A and B, a very convenient arrangment. The ends of the tubes are bent over, as shown at F and G, (fig. 6.) When connected up, the tube and bulbs should so support each other as to stand upright safely.

"J" is a U-tube similar to the last, but larger, having the limb next to I filled with $CaCl_2$, and the other with granular soda lime.

This serves as a guard tube to prevent moisture or CO_2 working back into the absorption apparatus from the aspirator. It can be used almost indefinitely without becoming exhausted.

"K" is an aspirator for sucking air slowly through the apparatus.

This must be arranged so that it can be easily attached and detached. It can be made from a five-pint acid bottle by boring a hole near the bottom with a pointed file dipped in turpentine, fitting a glass tube in this by a rubber ring and then attaching to this a rubber tube and pinch-cock.

Notes on the above Apparatus.—It is essential that none of the chromic acid solution come in contact with the rubber stopper or connections, as it would, of course, form CO_2. For similar reasons it is necessary that the glass stopcock in the funnel tube be free from grease of any sort.

A flask provided with a ground glass cap, into which the tubes are fused, may be substituted for the cork flask as described.

※ Liquids always absorb some CO_2, hence the volume of all absorbing liquids used in the purifying train must be small. The CO_2 absorbed is, however, given up again to a current of air passed through them for some time.

Setting up and Testing the Apparatus.—The connection tubes are united by short rubber tubes. These must be carefully tied with thread or wire, as it is essential that the whole apparatus be air tight. Rubber stoppers are, of course, the best, but good ordinary corks can be used if rolled soft and carefully bored and fitted. Sealing wax should not be used on these corks to make the joints tight, as it is liable to crack and leak unexpectedly. The potash bulbs and U-tube may be "capped" when disconnected, by short rubber tubes closed with bits of glass rod. These caps must always be removed for a moment and then replaced just before weighing, that the air pressure inside and outside the bulb may become equal.

If the ends of the glass tubes are heated until they draw together leaving only a small opening the size of a knitting needle, the rubber "caps" need not be used, provided the weighing is promptly done, as these small holes will not admit of any noticeable diffusion of moisture into the bulbs.

It is desirable to pass some CO_2 through the apparatus after first setting it up, in order to saturate any alkaline material present in the $CaCl_2$, etc. When this is done the weighed part of the train is, of course, omitted. Connect up the train, leaving out the parts H, I and J. Put a little marble in the flask, add a little dilute H_2SO_4 so as to generate a slow stream of CO_2. Let this run through the portion of the train remaining for about thirty minutes. Disconnect and wash out the flask, replace it, and then aspirate air until three or four litres have been slowly drawn through the apparatus.

Now connect up the whole train and attach the aspirator. Close the stopcock in the funnel tube of the flask and see if all connections are *tight*. This is shown if the water entirely stops running from the aspirator. Let in air cautiously by opening the stopcock in the funnel tube. Attach the soda lime guard-tube to the funnel tube and aspirate one or two litres of air carefully (not over one or two bub-

bles a second). Disconnect the bulbs and the U-tube, cap them, and wipe them carefully. Set them in or near the balance case until they attain its temperature (ten or twenty minutes). Uncap them a moment, replace the caps and then carefully weigh them. Replace them in the train and aspirate 1500 c.c. more, of air detach and reweigh them. The KOH bulb will lose (due to giving up moisture) and the U-tube will gain weight. The loss in one must equal the gain in the other. The total weight of the absorption apparatus must not change more than one-half milligram.

Treatment of the Carbon Residue from the Iron.—Transfer this to the flask C, using a little water if necessary to wash out the filter tube. The total amount of liquid in the flask must not exceed 20 c.c. Now dissolve four grams of chromic acid in 4 c.c. of water, and pour it into the flask through the funnel tube, following it with 2 or 3 c.c. of water to wash out the tube. Now put into the bulb of the funnel a quantity of concentrated H_2SO_4, equal to about two and a half or three times the volume of the liquid in the flask.

This volume can be estimated by pouring water into a second similar flask until it appears to contain the same amount of liquid as the first and then measuring the quantity used.

The acid used should be purified from any trace of organic matter that it may contain, by adding a little chromic acid to a quantity of it and then heating it to about 200° C for a few minutes. Let it stand till cool before using.

Now open the stopcock and run the acid slowly into the flask, being careful to avoid too violent action. When the acid is all in, shake the flask around carefully to mix the contents.

The evolution of CO_2 will begin at once. Finally heat carefully to boiling, so regulating the heat that the evolution of the gas does not take place too rapidly. The gas should not pass through the potash bulbs faster than 2 or 3 bubbles

per second. The boiling should be continued for two or three minutes. At the end of this time but little gas should be coming over through the bottles; but as some oxygen is likely to be given off by the chromic acid mixture, it is usually not possible to continue boiling till the evolution of gas ceases. Now withdraw the lamp and immediately open the stopcock of the funnel tube to admit air and prevent back suction. Connect the funnel tube with the soda lime guard tube, and let the apparatus cool a few minutes. Then aspirate carefully until a volume of air has been drawn through equal to seven or eight times the capacity of the apparatus.

Detach the absorption apparatus and weigh it. The total gain in weight will be the amount of CO_2 formed, and this multiplied by 0.2727 gives the amount of carbon in the sample taken.

The greatest care and "handiness" are necessary, but with skill duplicates should agree within 0.01 per cent.

The solution should not be brought to the boiling point too rapidly. By raising the temperature slowly time is given for the reaction and most of the carbon will be burned before the liquid begins to boil. If much unoxidized carbon is present in the boiling liquid particles of it are likely to be carried up on to the sides of the flask where they will adhere and so escape oxidation.

If white fumes form toward the end of the boiling, let the flask cool until they disappear before aspirating.

The foregoing method of determining carbon by combustion with chromic acid is very accurate if conducted carefully. It has the advantage of demanding no special or expensive apparatus.

THE DETERMINATION OF THE CARBON BY COMBUSTION IN OXYGEN.

In this method the residue from the solution of the iron in cupric potassium chloride is burned in a current of oxygen gas and the CO_2 produced absorbed by KOH solution as in the chromic acid method. The results are very accurate. At a red heat the combustion of the carbon is rapid. The carbon is not entirely burned to CO_2

some of it escaping as CO. In order to insure the complete oxidation of the CO as well as any other volatile compounds containing carbon, the products of combustion must be passed over red hot CuO.

As the carbon residue from the iron always contains sulphur and frequently chlorine, the gas from the combustion will contain SO_2 and Cl or HCl. As these would be absorbed by the potash bulbs it is necessary that they be removed before absorbing the CO_2. This is accomplished by passing the gas over hot lead chromate which holds the sulphur as lead sulphate and also some of the chlorine as chloride, and then over silver foil which will catch any chlorine escaping the lead chromate.

Apparatus and Reagents.—Oxygen gas: (see ultimate analysis of coal.) It is essential that this be free from any carbon compounds not removable by passing the gas through a solution of KOH as they would form CO_2 in the combustion tube.

It should be tested by passing about 500 c. c. through the purifier and hot tube as in an actual combustion. There should be no increase in the weight of the potash bulbs as this would indicate the formation of some CO_2.

If not pure it may be purified before entering the combustion train by passing the gas through a tube filled with CuO and heated in a second furnace. This will burn any hydrocarbons and the CO_2 formed will be removed by the purifying train.

If the oxygen is carefully made and kept in a clean gas holder this preliminary treatment is not necessary.

The gas must not be passed through long rubber tubes as it is liable to take up hydrocarbons from the rubber. Use glass tubes with short rubber connections.

FIG. 7 Oxygen Holder.

The gas holder shown in fig. 7 was designed by the writer some years ago; it has the advantage of keeping the gas at constant pressure, a point of some importance in combustion work as variations in pressure affect the rate of flow through the furnace.

A is a drum of tinned copper 14 inches in diameter and 24 high. It is provided with a stopcock, H, for drawing out the gas and a gauge, B, for showing the level of the water in the drum. I is an opening near the bottom of the drum for letting out the water when filling the tank with gas. When using the tank this opening is closed with a good rubber stopper. The gas is run into the tank through the cock H or by a tube inserted into I and small enough to allow the water to escape around it. The arrangement for forcing the gas out of the tank is as follows: Water is kept running into the cup, E, on top of the drum at such a rate as to overflow continuously through one of the side openings, F, into a sink. The head of water on the gas is determined by the opening selected, the others being closed by corks. From the bottom of this cup a pipe, D, runs down into the drum and into an interior cup, C, which fills with water and overflows through the pipe G, into the bottom of the tank.

It will be seen that the water will in this way fill the tank and force out the gas and yet the "head" on the gas will always be the difference in the level between the water in the cup E, and that in the cup C inside the tank and thus remain constant. The interior cup can be made smaller than shown in the figure; it is only necessary that it have volume enough to allow for the expansion and contraction of the gas due to the ordinary changes of temperature in the

laboratory. If too small the gas may force out the water and escape. The pipe, D, must be closed with a rubber stopper while the tank is being filled, or air will be drawn in by suction as the water escapes from I.
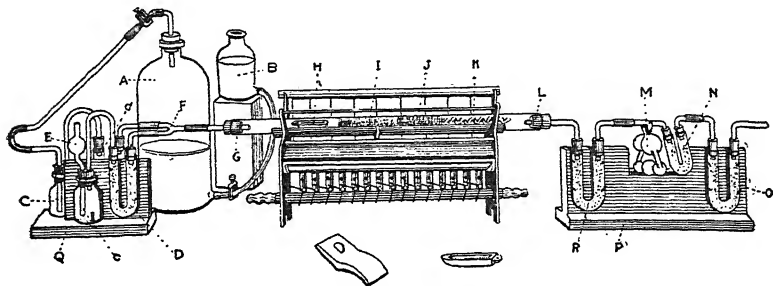
FIG. 8—Combustion Train for Carbon.

The Combustion Train.—Fig. 8 shows a simple arrangement of this apparatus as used by the students in the writer's laboratory. It requires no special supports except the wooden racks, Q and P, which can be made by any carpenter. The whole train can be detached and set on a shelf when not in use. The U tubes are held in place by wire finishing nails between which they slide. The nails are covered with small rubber tubing to keep them from contact with the glass. The combustion tube I is of Jena glass and is about 26 inches long and about half an inch internal diameter. The ends must project at least 3 or 4 inches from the combustion furnace so that the rubber stoppers G and L with which it is closed may not become heated and give off vapors. The tube lies in a trough of sheet iron lined with thin sheet asbestos.

Jena glass tubes distort on heating and cooling, so the trough carrying the tube must be large enough to allow perfect freedom for the tube to "twist." The tube lasts a long time without breaking if treated in this way, but if in any way confined or fastened it will crack immediately. The first eight or nine inches of the tube are left blank to hold the boat, H,

with the carbon residue, then a small plug of asbestos is inserted. Following this are eight inches of CuO.

The asbestos used in the apparatus should be boiled in HCl, washed, dried and ignited in order to remove traces of $CaCO_3$ or other carbonates sometimes present.

The "wire" CuO should be used; the ordinary granular oxide sometimes contains carbon and carbonates which, of course, renders it useless. The CuO may be made in the tube by putting in copper gauze or wire and oxidizing it in a stream of oxygen at a red heat, but this oxidation takes a very long time and good "wire" oxide can now be obtained which answers all purposes.

Following the CuO is a second plug of asbestos and then two inches of pure fused $PbCrO_4$, J. This must be in moderately coarse lumps from which all fine material has been sifted out with a 20 or 30 mesh sieve. It must also be neutral and free from alkaline chromates Then a third plug of asbestos followed by three and a half or four inches of pure sheet silver, K, rolled up loosely or made into a zigzag by folding two strips over each other alternately and drawing out the packet. The silver should be removed from the tube occasionally and heated red hot in coal gas or hydrogen to decompose the coating of AgCl which gradually forms on it and interferes with the absorption of the chlorine.

Preceding the combustion tube is the purifying train for air and oxygen. This is shown to the left of the figure. It is made in duplicate, one side for air and one for the oxygen. This is important as it obviates the necessity for considering this part of the train in estimating the volume of air that it is necessary to aspirate after the combustion is finished.

The smaller the volume of air which will carry all the CO_2 out of the combustion tube and into the potash bulb the less time will the analysis require and the less will be the danger of errors from insufficient purification of the air, variations in moisture of the air entering and leaving the potash bulbs, and imperfect absorption of the CO_2. For these reasons it is very desirable to keep the volume of the apparatus as small as possible.

The purification apparatus for air consists of the 2 oz.

bottle, C, containing a small amount of potash solution and the 8-inch U-tube, D, the first limb of which is filled with soda lime and the second with dried calcium chloride. The air enters the bottle, C, through the bulbed tube E, which dips into the liquid. The large bulb serves to prevent the liquid overflowing in case of any back pressure. The soda lime and the calcium chloride are separated in the tube by a plug of absorbent cotton. The space above the salts in the tubes should also be filled with absorbent cotton.

The apparatus for the oxygen is the same except that the large bulb, E, is omitted, the gas coming direct from the holder (here shown as the large bottle A). The oxygen and air are carried to the end of the combustion tube by means of the Y tube F. Each can be separately regulated by a pinchcock (not shown in the cut,) on the rubber tube connecting the U-tube and the Y-tube.

This purifying train is not soon exhausted and will serve for many combustions.

Following the combustion tube is the absorbing train consisting of the calcium chloride tube, R, the potash bulbs, M, with the guard tube, N, containing soda lime next to the potash bulbs and calcium chloride in the other limb, and finally the second guard tube, O, as in the chromic acid train. This tube must have the side containing the calcium chloride next to the first guard tube.

Testing the Apparatus.—1st. See that the connections are tight. This is tested as usual by attaching the aspirator. 2nd. Heat the combustion tube to dull redness. See that the heating proceeds slowly, using a small flame at first or the tube may crack. The portion of the tube occupied by the silver foil should not be made red hot. Connect up the train and pass about 500 c.c. of oxygen through the tube. Now aspirate air to the amount of seven times the estimated volume of the apparatus, detach the KOH bulbs with their guard tube and weigh them. Replace the bulbs and repeat

the process and again weigh the bulbs. If the change in weight does not exceed 0.5 milligram it proves the train to be in good condition and the oxygen free from any impurity which will affect the determination.

Determination of the Carbon.—The carbon is burned in a small platinum or porcelain boat. This should be heated red hot and allowed to cool shortly before using in order to burn off any adherent dust or carbonaceous matter. The felt carrying the carbon is now removed from the filtering tube in the manner already described. Now holding the disc by its stem, detach the felt by a wire or knife blade and drop it into the boat. Wipe off any trace of carbon adhering to the tube with a tuft of ignited asbestos and add it to the boat. The boat and its contents can now be dried at 100° C till excess of moisture is removed. When it is dry withdraw the stopper from the empty end of the combustion tube and immediately introduce the boat, pushing it up until it touches the asbestos in front of the CuO. Immediately insert the stopper and connect up the train with the recently weighed KOH bulbs. Start a slow aspiration of air (about one bubble a second). Now light the burners under the portion of the tube occupied by the CuO, the $PbCrO_4$ and the Ag, turning those under the two latter low. As soon as the CuO is red hot and the $PbCrO_4$ just visibly red (the silver must not be red hot) turn on the burners behind the boat and then under it. At the same time turn on the oxygen in place of air maintaining such a rate of flow as will cause the gas to bubble through the KOH bulbs very slowly. The oxygen will run in through the purifying train much more rapidly but as the gas is burned to form CO_2, only the unused oxygen and any intermixed nitrogen will escape through the bulbs. The carbon in the boat will begin to glow when the oxygen reaches it.

The admission of oxygen must not be too rapid or the asbestos may fuse and make trouble by protecting carbon from combustion. The maximum rate must be learned by experience. From 300

to 500 c.c. of oxygen will be needed for each combustion. The tube surrounding the boat should be brought to a red heat. The carbon will burn out in about ten minutes.

The end of the combustion is usually indicated by the sudden cessation of the "glow." After this happens, continue the heat and the gas supply for about two minutes to insure the completion of the combustion. Now turn off the oxygen, turn on the air and start the aspirator. Air may be drawn through the bulbs at the rate of two or three bubbles a second without danger of CO_2 passing unabsorbed. The amount of air required varies with the apparatus, but seven times the volume of the train is sufficient. With a compact train such as has been described, one litre is usually ample. While the aspiration is continuing, the burners can be turned out and the tube allowed to cool, unless a second combustion is to follow immediately, when only that part occupied by the boat should be allowed to cool. In this case as soon as the aspiration is finished a new boat may be introduced for a second combustion, of course using a second set of weighed KOH bulbs and guard tube. After the combustion is finished the KOH bulbs with their guard are detached and weighed, the gain in weight being CO_2.

It is necessary to aspirate till the oxygen in the train is replaced by air so that the bulbs may be filled before and after the combustion with gas having the same specific gravity. If the bulbs are filled with oxygen before the combustion the air aspiration may be omitted and the CO_2 washed out of the tube by oxygen, the bulbs being weighed filled with oxygen at the end. This procedure is wasteful of oxygen and in a train arranged to reduce the necessary amount of aspiration to a minimum saves but little if any time. The combustion method as above described is rapid and convenient and the results are very accurate. The points needing special attention are the regulation of the air and gas flow and the temperature of the different parts of the tube. The CuO must be bright red hot, the $PbCrO_4$ barely red and the silver foil under a red heat. Large connecting tubes should be avoided and by limiting the aspirating to the amount that is strictly necessary, the difficulty of obtaining constant weight of the KOH bulbs is reduced to a minimum. The bulbs must be weighed at approximately the same room temperature both before

and after the combustion. Changes in this respect as well as extensive changes in the barometer will affect the apparent weight owing to the great difference in specific gravity of the brass weights and of the absorption apparatus. For instance, an increase of temperature of 10° C, and a drop in the barometer of three tenths of an inch acting together might change the apparent weight of an absorption bulb and tube weighing 75 grams and having a mean sp. gr. of 1.5 by about 2.3 milligrams. Of course this would be an extreme case but it shows the importance of considering this source of error. Marked changes in the moisture in the air will also greatly affect the weighings both by affecting the specific gravity of the air and more important by affecting the surface moisture of the apparatus. If the air is at or near the "dew point" it is impossible to do accurate work. It has been proposed to reduce these errors by counterpoising the bulbs by a pair of "dummy" bulbs so that variations would affect both alike. But this involves errors in maintaining the conditions alike for the two sets that may exceed those sought to be corrected. Care and watchfulness are all that are necessary to render the weighings sufficiently satisfactory in the ordinary method.

Instead of conducting the combustion in a glass tube it can be done in a platinum tube or in a porcelain tube or finally in a platinum crucible, using in this case a very ingenious apparatus devised by Prof. Shimer. The following references cover these methods.

Shimer. Carbon Combustions in a Platinum Crucible. Jour. Am. Chem. Soc., July 1899.
Sargent. Combustion in a Porcelain Tube with a Modified Train for very rapid Work. Jour. Am. Chem. Soc., May, 1900.
For Combustion in a Platinum Tube, see Blair, The Chemical Analysis of Iron, 4th Edition.

THE DETERMINATION OF CARBON IN STEEL BY COLOR.

This method is in general use in steel works. It depends upon the fact that when steel is dissolved in dilute HNO_3 a brown compound containing the carbon forms. This goes into solution, on boiling, coloring the liquid more deeply as the percentage of carbon is higher. Pure iron dissolves in HNO_3 sp. gr. 1.2, giving a nearly colorless solution, and from which every trace of color is removed by moderate dilution.

The color produced by the carbonaceous matter is rapidly altered by light. Its depth depends somewhat on the mode of solution, the concentration of the acid and the kind of steel, hence the process must be conducted strictly according to rule to get concordant results.

There is required: First, a standard steel, which must be of exactly the same kind as that to be tested, and also similar in its composition and of approximately the same carbon percentage. The

carbon in this must have been accurately determined gravimetrically. Second, nitric acid of sp. gr. 1.2 perfectly free from chlorine, the least trace of which will seriously alter the color of the iron solution, making it more yellow. The above strength corresponds to 1 volume of concentrated acid to 1 volume of water. Third, comparison tubes of clear white glass, graduated in $\frac{1}{10}$ c.c., and of exactly equal diameters.
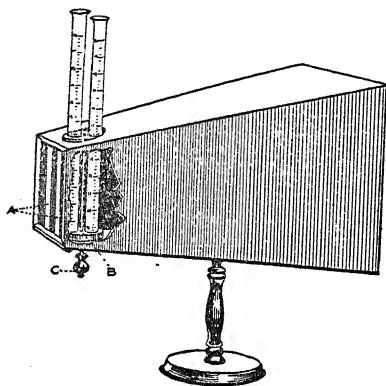
FIG. 9. Box for comparing color tubes

For comparing the colors an arrangement such as is shown in fig. 9, is convenient. It consists of a wooden box open at one end and closed by a sheet of ground glass at the other. The glass is covered with black paper, except the two slits, A, before which the tubes are placed and compared by the observer, who looks into the large end of the box. The tubes are carried by a little rack, B, which can be revolved by turning the knob, C, and the tubes thus reversed without taking them out of the box. This reversal of the tubes is important, as the eye will usually see the right hand tube darker. In the absence of such a "camera" a piece of wet paper on a window makes a good temporary back ground.

If the steel contains much sulphur the solution will be slightly *turbid* from free S. Comparison is difficult in this case.

The volume of acid used should bear some relation to the percentage of carbon present. The amount of metal taken must be increased when the carbon is low. It is essential that both standard and sample be treated exactly alike, as to the amount of sample taken, time of heating and volume of acid. It is especially important that the standard and the sample should have undergone the same "heat treatment" in their manufacture. Only the combined carbon is determined by the color method, any free carbon present not affecting the color.

Process.—Weigh 0.2 gram of the steel and of the standard, each into a 6-in. test tube. Add to each tube a measured volume of cold HNO_3 sp. gr. 1.2 using the following amounts: For steels with not over $\frac{1}{10}$ per cent. carbon, 4 c.c.; from $\frac{2}{10}$ to $\frac{5}{10}$

per cent., 6 c.c.; from $\frac{5}{10}$ to 1 per cent., 8 c.c.; and over 1 per cent., 10 c.c.

Stand the tubes in cold water till violent action ceases. Then set them in boiling water and heat until the solution is perfectly clear and no more fine bubbles of gas appear. Keep the mouths of the test tubes closed loosely by little glass bulbs or balls to prevent drying of the iron salts on the sides of the tubes. The time required will be from 15 to 30 minutes, according to the percentage of carbon in the steel. Now cool the tubes in water. Add an equal volume of water to each and pour into the comparison tubes. Dilute carefully until the colors match. The percentages of the carbon will be to each other as the volumes of the liquids in the tubes.

Where a number of steels are to be tested at once it is convenient to dilute the standard until each c.c. represents some definite percentage of carbon, and then match it with the others, so that the readings in c c. can be readily converted to per cents. For example, if the standard contained 0.38% C, dilute it to 19 c.c., then if a comparison showed the unknown steel to read 16 c.c. it would obviously contain 0.32% carbon.

Where the color carbon process is used on steels of comparatively uniform contents, it is usual to take 10 c.c. of acid and then enough of the sample to give a sufficiently marked color with this amount; for example 0.5 gram of steel and 10 c.c. of acid. In the case of very low carbon steel (under 0.2 per cent,) 1 gram of steel may be dissolved in 20 c.c. of acid.

The color process can be applied to pig iron and gives an approximate determination of its combined carbon. In this case a solution of the sample and of the standard must each be filtered through a small filter and the solutions compared. Filters of the same size and a pig iron standard must be used.

The use of permanent standard colors, either organic or inorganic such as the mixed chlorides of iron, copper and cobalt, has been tried. This is not advisable as it does not provide for the variations in color due to slight differences in the treatment, as well as does the treatment of standard and sample together. For these methods see Trans. Am. Inst. Min. Engs. Vol. I, p. 240, and Vol. XVI, p. 111.

For very low carbon steels the color is faint and uncertain. An

alkaline method has been used on such metals.   See Stead. Jour. Iron and Steel Inst. 1883, No. 1, p. 213.

THE DETERMINATION OF THE GRAPHITE IN PIG IRON.

When pig iron is boiled with HCl or dilute HNO_3 the combined carbon is converted into solid, liquid, or gaseous hydrocarbons; while the graphite is all left insoluble.   The non-volatile hydrocarbons are soluble either in alkalis, in alcohol, or in ether.   The graphite or uncombined carbon is not acted upon by any of these reagents but remains in the residue as a black mass.   The residue may also contain hydrated silica and frequently titanium carbide and free sulphur. The silica holds water tenaciously and cannot be thoroughly dehydrated below a red heat.   Titanium carbide is decomposed by HNO_3 but not by HCl: while sulphur is separated by dilute HNO_3 but not by HCl. Graphite is not at all oxidized by HNO_3, sp. gr. 1.2.   The use of nitric acid is preferable with gray irons low in combined carbon, while HCl is better for white iron high in combined carbon and for ferro silicons as these only dissolve with difficulty in HNO_3.   The carbon in the residue can only be accurately determined by combustion.

Shimer.   Jour. Am. Chem. Soc. Vol. XVII, p. 873.
Drown.   Trans. Am. Inst. Min. Engs. Vol. 3, p. 41.

Process.—Treat 2 grams in a beaker with 50 c.c. of HCl, sp. gr. 1.12.   Cover and boil briskly for 30 minutes.   Dilute, filter onto an asbestos filter and wash with hot water until all iron salts are removed.   Then pour on a little HCl and wash again with water.   Now wash the residue with a solution of caustic soda, then with water, then with alcohol, then with ether, and finally with cold water, then hot water till every trace of ether is extracted.   Now transfer to the carbon apparatus and determine the carbon with chromic acid and sulphuric acid, or by combustion in oxygen.

This complicated washing is required to remove the solid and liquid hydrocarbons which are likely to form and are insoluble in water alone.

The ether must be followed by cold water; if hot water were added at once, it would make the ether boil and might throw the carbon out of the filter tube.   Nitric acid of sp. gr. 1.135 can be substituted for HCl with such irons as are readily dissolved by it.   If a little HFl is added to the solution after the metal is dissolved it will frequently greatly facilitate the filtration by preventing the sep-

aration of silica in a gelatinous form. By using a sufficient quantity of acid of the right specific gravity, most of the silica will usually remain in solution.

DETERMINATION OF THE GRAPHITE BY DIRECT WEIGHING.

This method gives satisfactory results on many irons. It is quite generally used as a rapid method. It should be checked by the combustion method when applied to kinds of iron not previously tested.

The residue is dried at 100° C, and then burned and the loss of weight assumed to be carbon. Any sulphur or water that the residue contains will, of course, be rated as carbon.

Process.—Weigh out 2 grams of the drillings into a 250 c.c. beaker. Add 100 c.c. of HCl sp. gr. 1.1 or of HNO_3 sp. gr. 1.135. Boil gently till all action ceases. Keep the beaker covered to prevent evaporation and concentration of the solution which may cause the separation of silica. Finally add three or four drops of HFl and boil again. Prepare a "Gooch" perforated crucible as follows: First, heat, cool and weigh it, second, fit into the bottom of the crucible a disc of ashless filter paper and dry the paper and crucible at 100° for twenty minutes and weigh again. Filter the solution through this crucible in the ordinary way, transfering the residue with cold water. Then wash the residue with hot dilute HCl, then with hot water, and then with a five per cent. solution of NH_4OH. When the filtrate runs through colorless finally wash with a mixture of equal parts of alcohol and ether. Now dry the crucible and contents at 100° C to constant weight which will take from ten to twenty minutes. Now set the crucible over a Bunsen Burner flame and burn off the residue. When all the carbon has burned away, weigh the crucible again.

By subtracting the weight of the crucible with the fiter paper, from the weight of the crucible plus the filter paper plus the residue, the weight of the residue is obtained. Subtracting the weight of the empty crucible from the final weight of the crucible plus the incombustible portion of the

residue, gives the silica and other mineral matter with the carbon. Subtracting this remainder from the total weight of the carbonaceous residue, gives the weight of the graphite.

Instead of using a "Gooch" crucible, two small tared filters can be taken and then the residue burned out in an ordinary crucible, but this is not nearly so convenient.

The above method is essentially that given by A. B. Harrison in Methods of Iron Analysis used around Pittsburg, 2nd Edition, p. 85. For variations of the method, and discussion of the results, consult:

Daugherty. Chem. News. Sept. 8, 1899.

Crobaugh. Jour. Am. Chem. Soc. 1894 p. 104.

Auchy. Jour. Am. Chem. Soc. 1900 p. 47.

THE DETERMINATION OF TITANIUM.

Titanium usually occurs in iron ores as menaccanite and is most frequently found in magnetites.

Titanium occurs in pig iron as carbide and sometimes, especially in manganese alloys, as nitrocyanide forming small copper-red crystals with metallic lustre.

If titaniferous iron ores are heated with concentrated HCl most of the TiO_2 goes into solution, provided the material is reduced to an extremely fine powder.

Rutile, ignited TiO_2 and other compounds of titanium, which are not attacked by HCl, can be dissolved after fusion with acid potassium sulphate ($KHSO_4$). The fusion is slowly but completely dissolved by cold water. The titanic acid, iron and other bases go into solution as sulphates, while any silica present is left as a residue. Should phosphoric acid be present, some TiO_2 is liable to remain with the SiO_2 as phosphate.

When ores or other minerals containing titanium are fused with a large excess of sodium carbonate, they are completely decomposed, provided they are very finely pulverized. When the "melt" is boiled with water till thoroughly disintegrated, any sodium phosphate, sodium aluminate or sodium silicate present, go into solution, while sodium titanate being insoluble remains with the oxide of iron and other bases. The separation is complete in the case of the phosphates; in the case of the silicate and aluminate only partial.

The residue of titanate, etc., is soluble in HCl or even more readily in hot H_2SO_4. This solution may be freed from silica by evaporation with H_2SO_4 till HCl is expelled and the silica dehydrated. This treatment will dissolve any TiO_2 the HCl does not attack. On dilution with water the TiO_2 and the bases go into solution as sulphates, while the SiO_2 is left insoluble and free from TiO_2.

TiO_2 is precipitated (as a hydrate) from slightly acid solutions on boiling. In order that the precipitation may be complete, the solution should be dilute and not contain more than one-half per cent. of free acid. The boiling must be prolonged and not more than traces of phosphoric acid be present. If ferric oxide, alumina or phosphoric acid are present in the solution they are invariably partially precipitated with the TiO_2.

The precipitate has a tendency to adhere to the glass, and is fine and difficult to filter and wash.

The precipitated titanic hydrate is only soluble with difficul in mineral acids, and is insoluble in acetic acid.

Solutions containing TiO_2 are completely precipitated by ammonia. TiO_2 is also completely and promptly precipitated on boiling from solutions containing sodium acetate and a large excess of acetic acid (15 to 20 per cent.), provided *ferric salts* are not present. Any phosphoric acid present will come down with the TiO_2. As alumina is not precipitated under these conditions, TiO_2 can be separated from it in this way. A repetition of the precipitation is necessary to get a complete separation.

See Gooch. Chem. News, Vol. LII, p. 55.

The best solvent for hydrated TiO_2 is a mixture of eight volumes of concentrated H_2SO_4 and three volumes of water, heated to its boiling point.

If this solution is concentrated by boiling until the water is all expelled, the TiO_2 will separate again in a form which cannot be redissolved; hence, in the process which follows *avoid too long heating of the sulphuric acid solutions.*

If ignited TiO_2 is heated with HFl, a portion of the Ti will be volatilized as fluoride, but if the TiO_2 is first moistened with H_2SO_4 and then treated with the HFl none of the Ti will be volatilized on drying and igniting the mixture.

Process for Iron Ores.—Take one or two grams (the ore must be ground to an impalpable powder), put into a small covered beaker, add 30 c.c. of concentrated HCl, and boil gently till the iron appears to be dissolved. Now add 10 to 15 c.c. of dilute H_2SO_4 (1 to 4 of water by volume), boil down till the HCl is all expelled and fumes of H_2SO_4 just begin to appear, being careful to avoid over-heating. Cool the liquid and add 25 c.c. of water, then boil till all the iron salts are dissolved; filter from the residue and wash. Dry and save the *residue* to be examined for TiO_2. It is usually free from it, but sometimes may contain a considerable amount.

Dilute the filtrate to 250 to 300 c.c. Add NH_4OH carefully until the precipitate formed at first dissolves very slowly on stirring. Now warm the solution and add a solution of sodium sulphite slowly, and only a little at a time.

The deep color produced by each addition will rapidly disappear as the iron is reduced. The sulphite solution is prepared by dissolving the salt in five parts of water, then adding H_2SO_4 to the solution until it reacts distinctly acid.

Should the iron solution grow turbid while adding the sulphite, and a precipitate form, add a few drops of HCl to clear it, and continue with the sulphite solution, giving more time for the reaction. The solution should not be heated to boiling or TiO_2 will separate as a white, milky precipitate, not redissolving on the addition of a few drops of HCl, and making the completion of the reduction difficult to distinguish though doing no harm otherwise. By the time that 40 to 60 c.c. of the sulphite solution have been added in this way the liquid should be colorless and smell strongly of SO_2. If it is still colored showing that the ferric salts are not all reduced, continue the warming till it becomes colorless, as it is necessary that the reduction be complete. Now add 50 to 60 c. c. of acetic acid, and then 20 grams of sodium acetate, and boil the solution vigorously for three minutes. The TiO_2 will separate as a flocculent precipitate. Let this settle, filter it off and wash it with hot water. Call this precipitate A; it contains all the TiO_2 in the solution but is impure, containing phosphorus and usually some iron.

Treatment of the Residue.—Put the filter and residue into a platinum crucible and ignite until all carbon is burned off. Now add ten times its weight of dry Na_2CO_3 and fuse over a blast lamp until thoroughly decomposed. Cool, add water and boil until the melt is thoroughly disintegrated and the insoluble portion is flocculent. Filter and wash with hot water. Wash the residue on the filter off into a beaker with a little water. Let it settle and decant the water through the filter again. Dissolve the little adhering residue from the filter with a few drops of HCl, running it through into the beaker containing the rest. Add a little HCl to the contents of the beaker, then add 10 c.c. of dilute H_2SO_4 (1 to 4) and boil

The precipitated titanic hydrate is only soluble with difficulty in mineral acids, and is insoluble in acetic acid.

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The deep color produced by each addition will rapidly disappear as the iron is reduced. The sulphite solution is prepared by dissolving the salt in five parts of water, then adding H_2SO_4 to the solution until it reacts distinctly acid.

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the mixture, everything should dissolve. Evaporate the liquid until all the HCl is expelled, being careful to avoid too great concentration which may precipitate the TiO_2. Now cool and add 25 c.c. of water, boil and filter from the SiO_2, which will be free from TiO_2. Now dilute the filtrate to 150 c.c., add NH_4OH till a slight precipitate forms. Redissolve this with a little HCl, and then add 10 c.c. of the sulphite solution. If a precipitate now forms drop in HCl till it dissolves. Now heat the liquid gradually and as soon as the solution is colorless add 30 c.c. of acetic acid and 10 grams of sodium acetate. Boil the solution for three minutes and if any TiO_2 separates, filter it off and wash it with hot water. Call this precipitate B.

Treatment of the Impure Precipitates.—Put the filters with precipitates A and B into a platinum crucible. Burn off the filter papers completely, and weigh the impure TiO_2. Add ten times its weight of dry Na_2CO_3 and fuse the mixture. Boil the fusion with water until it is completely disintegrated; then filter and wash. Now wash the residue off the filter into a beaker; let the liquid settle and decant the clear liquid back through the filter (the object of this is to get the residue into the beaker, yet have very little water present).

Pour a little concentrated HCl onto the filter paper, letting it run through into the residue in the beaker, (this dissolves most all of the TiO_2 adhering to the paper). Finally burn the paper at as low a heat as possible and add the ash (still retaining a trace of TiO_2) to the beaker. Dissolve the contents of the beaker in concentrated HCl, then add 10 or 15 c.c. of dilute H_2SO_4 and evaporate as before, cool and dilute with 25 c.c. of water, boil, filter and wash. Dilute the solution to 250 c.c., nearly neutralize with NH_4OH, add 20 c.c. of the sulphite solution to reduce the small amount of iron present, and then precipitate the TiO_2 with sodium acetate and acetic acid as in the treatment of the original solution of the ore. The second precipitate of TiO_2 is pure

and should be white. It is dried, ignited intensely and weighed. The ignition should be repeated and the precipitate re-weighed until its weight is constant. The TiO_2 should be light colored after ignition.

In the above process the H_2SO_4 serves two purposes. It separates SiO_2, and when concentrated to the right strength it is the most powerful solvent for TiO_2, dissolving the oxide even after it has been moderately ignited.

The above process is accurate and satisfactory. For a description of a slightly different method, based on boiling down the TiO_2 see an article by Charles Baskerville, Jour. Soc. Chem. Ind. 1900, p.419.

PROCESS FOR ORES NOT ATTACKED BY HCl.

Prepare pure bisulphate of potash by melting the salt in a platinum dish or crucible until all boiling ceases and it is in quiet fusion. When cool, pulverize it and keep it in a tightly stoppered bottle.

Mix the very finely pulverized ore with 15 times its weight of the bisulphate in a large platinum crucible and heat gently till the mass melts. Raise the temperature to a low red gradually until white fumes begin to come off, and keep the mass in quiet fusion 20 or 30 minutes. Avoid too high a temperature or the H_2SO_4 will be driven off and the fusion spoiled. Insert a platinum wire into the melted mass and let the crucible cool. The mass will generally detach itself from the crucible and can be lifted out by the wire. Now put crucible and cover into a beaker. Add a considerable amount of cold water. Hang the lump of fused material in the water and let it soak out. Everything will gradually dissolve except the SiO_2, though it may take 12 hours. Now filter from the residue of SiO_2 and proceed as with the ordinary solution.

The bisulphate fusion may be made to dissolve more rapidly, if after cooling in the crucible a little concentrated H_2SO_4 is added, and the whole again heated until it melts. On again cooling, the mass will be pasty and dissolve more rapidly. (Kennedy).

See Drown, Trans. Am. Inst. Min. Engs., Vol. X, p. 137.
Jennings, Eng. and Min. Jour., Vol. XLV, p. 475.

Process for Iron and Steel.—The metal should be dissolved in HNO_3 sp. gr. 1.2. A little HCl may be added to assist the solution. Evaporate to dryness, bake the residue and then add HCl to the dry residue and proceed exactly as with an ore.

DETERMINATION OF TITANIUM BY COLOR.

When hydrogen peroxide (H_2O_2) is added to a sulphuric acid

solution of titanium, a yellow-brown coloration is produced, the intensity of which is proportional to the amount of TiO_2. This is a very delicate qualitative test and has been made the basis of a color method. The results are satisfactory for small percentages. The solution of TiO_2 must be very dilute. The color is probably due to the formation of TiO_3. It is distinctly shown with less than .02 milligram TiO_2 to the cubic centimeter of the liquid. As HFl discharges the color it must be entirely absent. As some commercial hydrogen peroxide is said to contain fluorine as an impurity, it should be tested before being used in the process. Ammonium salts in the solution also interfere by decomposing the H_2O_2. Chromium, vanadium and molybdenum salts also produce colored compounds when treated with H_2O_2 and must be absent. Iron salts do not prevent the formation of the color, but as they have a color of their own they modify the tint. The solution should always contain the same amount (5 per cent.) of H_2SO_4.

A. Weller. Berl. Ber. XV, 2592.
Dunnington. Jour. Am. Chem. Soc. XIII, No. 7.
Noyes. Jour. Am. and App. Chem. Vol. V, p. 39.
Wells. Trans. Am. Inst. Min. Engs. Vol. XIV, p. 763.
Hillebrand. Jour. Am. Chem. Soc. 1895, p. 718.
Baskerville. Jour. Soc. Chem. Ind. 1900, p. 419.
Brakes. Jour. Soc. Chem. Ind. 1901, p. 23.

PROCESS FOR ORES.

Solutions Required.—Standard TiO_2. Ignite pure TiO_2 at a dull red heat to constant weight. Weigh 0.5 gram of the anhydrous powder. Put this in a platinum crucible with 5 grams of pure potassium bisulphate. Melt cautiously and keep at a low red heat for from five to ten minutes until the TiO_2 all dissolves and the liquid becomes clear. Partially cool the crucible and add 5 c.c. of concentrated H_2SO_4, then heat again till the mass liquifies. Cool and put the crucible and all into 200 to 300 c.c. of water containing 5 per cent. of H_2SO_4. When the fusion is dissolved wash and remove the crucible. The TiO_2 should dissolve to a clear solution. If any residue remains, filter it out, wash and weigh it and deduct it from the TiO_2 taken, using the difference in calculating the standard of the solution. Finally dilute the solution with five per cent. H_2SO_4 till 1 c.c. contains 1 milligram of TiO_2. Check it by precipitating and weighing the TiO_2 from 20 c.c.

This can be done by the regular gravimetric process. After weighing, the TiO_2 should be tested for SiO_2, by treating it with a little H_2SO_4 and HFl, igniting and weighing the residue. Any loss will be SiO_2.

Standard Solution of $Fe_2(SO_4)_3$.—Take 50 grams of crystalized ferrous sulphate. Add 100 c.c. of water and 50 c.c. concentrated H_2SO_4. Heat to boiling and when the Fe SO_4 is all dissolved, add HNO_3 drop by drop till the iron is all oxidized to the ferric state as is shown by the sudden disappearance of the brownish-black color. Concentrate the solution until it becomes pasty, stirring vigorously to prevent bumping. Add 50 c.c. more H_2SO_4 and heat with continous stirring until fumes of H_2SO_4 begin to come off. Now cool, add 200 c.c. of water and boil till the ferric salt is all dissolved. Dilute the solution to about 1 litre. Determine the amount of iron in 10 c.c. of this solution as in the iron assay.

Process for Ores.—Take 0.5 gram of the very finely pulverized sample and fuse it with 5 grams of $KHSO_4$. Keep it at a red heat for at least ten minutes, in which time all the TiO_2, Fe, etc. should dissolve in the melted salt. The addition of 1 gram of NaFl is said to help the solution, but in this case the heating must be continued until every trace of fluorine has been expelled. Cool the solution, add 5 c.c. of H_2SO_4, melt again and finally cool and put the crucible into a beaker with 200 c.c. of water containing 5 c.c. of H_2SO_4. Warm the contents of the beaker to about 90° C., and stir till the iron salts are all dissolved. Filter from the residue and dilute the filtrate to 250 c.c. with 5 per cent. H_2SO_4. If the residue is dark colored it should be tested for titanium by refusion.

To Estimate the Titanium.—Put 50 c.c. of the solution (equal 0.1 gram of ore) into a wide "Nessler" tube. Into a second similar tube put as much of the standard iron solution as will contain an amount of iron equal to that in 0.1 gram

of the ore and dilute this to 50 c.c. with 5 per cent. H_2SO_4. Add to each tube 5 c.c. of hydrogen peroxide and then add standard TiO_2 solution from a burette to the second tube till the color produced matches that in the first tube. From the volume of the TiO_2 solution used, calculate the amount of titanium added to the second tube which will be the same as that in 0.1 gram of the ore.

Four milligrams of TiO_2 is as much as can be estimated in 50 c.c. of liquid. Above this amount the increase of color with addition of more TiO_2 is not sufficiently marked. This would correspond to 4 per cent. in the ore. Higher percentages should be estimated gravimetrically.

The addition of the iron to the standard is necessary in order that the modification of the titanium color by the iron may be the same in the standard as in the ore.

THE DETERMINATION OF NICKEL IN STEEL AND IRON.

Nickel steel contains several per cent. of nickel. Nickel also occurs in small traces in some pig irons. Ferro-nickel may contain 30 per cent. or more. In the determination of nickel the first step is the separation of most of the iron. This can be done by precipitating the iron as basic acetate as in the manganese determination, but as the precipitate will always carry down some of the nickel it is necessary to repeat the precipitation several times to secure a good separation. The following method which depends upon the solubility of ferric chloride in ether is much more satisfactory. If a solution of ferric chloride in HCl is shaken up with sulphuric ether most of the iron will go into the ethereal solution while the chlorides of nickel, copper, manganese, cobalt and aluminum remain entirely in the aqueous solution. The conditions for securing a good separation are as follows: 1st, the chlorides must be dissolved in HCl of between sp. gr. 1.1 and 1.13; 2nd, the volume of the solution must be small, not exceeding 50 c.c.; and 3rd, the ether must be free from alcohol and must be saturated with HCl, by previously shaking it up with 5 to 10 c.c. of the concentrated acid. Finally, sulphates are said to interfere with the ether separation and if present, as is sometimes the case in applying the process to ores, must be removed. In this case the iron can be precipitated by NH_4OH and then dissolve in HCl and the ether separation applied to this solution. Part of the nickel will be in the filtrate from the iron and must be added to that left after the ether extraction.

Process: Separation of the Iron.—Dissolve 1 or 2 grams of the drillings in 30 c.c. of dilute HCl (1:1) in a small covered beaker. When dissolved, warm and add gradually 1 or 2 c.c. of HNO_3 to oxidize the iron. Evaporate the solution to about 10 c.c. Cool it and pour it into a separatory funnel of about 150 c.c. capacity and having a very short stem. Wash out the beaker with warm HCl of 1.13 sp. gr., transferring all the solution to the funnel. To keep the volume small, use successive small portion of 5 or 6 c.c. of the acid, in washing. The total volume of solution in the funnel should not exceed 40 c.c. Now cool the funnel and its contents and cautiously add 45 to 50 c.c. of ether previouly saturated with

HCl. Put in the stopper and shake the funnel vigorously for five minutes, keeping it cool by holding it under running water from a tap. Now set the funnel in a rack and let it stand until the ether separates and the line between the two layers of liquid is sharp. Then take out the stopper carefully and draw off the aqueous solution down to the stopcock, being careful to empty the tube. Now add 5 or 6 c.c. of HCl sp. gr. 1.13 to the ether in the funnel and shake it up again. Let it separate as before and draw off the acid adding this to the first extract. A second washing may be necessary if the steel contains over 5 or 6 per cent. of nickel, but with ordinary nickel steel one is sufficient. It is desirable to use as little acid as possible in the washing as it takes up some iron from the ether and increases that to be subsequently removed from the aqueous solution.

During the whole operation the ether and the funnel should feel cool to the hand; if allowed to become too warm, the vapor pressure may blow the stopper out of the funnel. The ether solution of $Fe Cl_3$ in the funnel may now be thrown away, or kept for the recovery of the ether by distillation. The aqueous solution contains some dissolved ether, a little ferric chloride (which should not exceed 2 per cent. of that in the original solution) and the whole of the chlorides of Ni, Co, Mn, Al and Cu. Set the beaker containing this solution on a water bath or hot plate and heat it until the ether is expelled. As the ether vapor is inflammable and heavy a little care must be taken that it does not catch fire. Keep the beaker covered while the ether is boiled off. After the ether is expelled, dilute to about 200 c.c. Add from 2 to 3 c.c. of bromine water and then a decided excess of NH_4OH. Boil till the $Fe(OH)_3$ separates well. Filter it off, wash the precipitate once with water, then wash it back into the beaker redissolve it in HCl and precipitate a second time with NH_4OH after adding bromine as before. The second precipitate is practically free from nickel unless the amount in the steel is very large, in which case a third precipitation

should be made. Combine the ammoniacal filtrates, boil off the excess of NH_4OH and add HCl till the solution is distinctly acid. If the metal contains copper it must now be separated by passing H_2S through the acid solution for some minutes. Filter off the CuS and concentrate the filtrate to 100 c.c.

In this filtrate which is free from iron, the Ni can be determined either gravimetrically or volumetrically.

The addition of bromine in the above process has for its object the precipitation of manganese with the ferric hydroxide.

The completeness with which Mn is precipitated by bromine and ammonium hydrate depends upon the amount of NH_4Cl in the solution, when this is large as in the above process only a very little of the Mn will come down, most of that present remaining in the solution.

If the amount of Mn present is considerable and it is desirable to separate it with the iron, most of the free HCl must be neutralized with Na_2CO_3 and Br added and then about 5 c.c. of NH_4OH.

Proceeding in this way very little of the Mn will be left in the solution. Hydrogen peroxide acts in the same way that bromine does, but ammonium persulphate will precipitate the Mn much more effectively from a solution containing NH_4Cl.

The effect of NH_4Cl in preventing the precipitation of Mn by bromine and ammonia is largely overcome by the presence of a sufficient excess of sodium acetate; where this reagent can be used in the solution, this method of separating Mn is useful.

Gravimetric Determination.—Add NH_4OH until the solution is just distinctly alkaline, carefully avoiding much excess. Now heat the liquid and pass a current of H_2S through it until it is saturated. The Ni separates as NiS and any manganese present as MnS. Now add acetic acid, using about 4 c.c. in excess of that necessary to neutralize the liquid. This will dissolve the MnS but not the NiS. Filter off the NiS on a small filter and wash it thoroughly with hot water. Carefully ignite the filter and precipitate in an open porcelain crucible, burning off the paper at as low a heat as possible and continuing the heating until the NiS is converted to NiO. Finally ignite intensely, cool and weigh.

As the NiO is easily reduced to a lower oxide, it is important to keep the crucible uncovered and to avoid contact with any reducing gas. After the paper and sulphur are burned off it is important that the NiO be intensely ignited or it may retain sulphates formed during the preliminary roasting. After weighing the NiO it is well to add a few drops of HNO_3 to reoxidize any reduced Ni. Dry it off and ignite and weigh again.

The Volumetric Determination of the Nickel with Potassium Cyanide.—This process depends upon the fact that when KCN is added to an ammoniacal solution containing nickel, a double salt, $K_2Ni(CN)_4$, is formed. In order to show when an excess of the KCN has been added a little silver iodide is formed in the liquid. This is insoluble in ammonium hydrate and in a solution of the above double salt, but is at once dissolved by an excess of KCN, a double silver potassium cyanide being formed.

$$2KCN+AgI=KAg(CN)_2+KI.$$
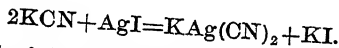
As the amount of the AgI present is always the same, the small amount of the KCN solution required to dissolve the silver salt is determined once for all and then deducted from the volume of the liquid used in the titration of the nickel solution, the remainder being that required for the nickel. Only enough of the AgI should be present to give a marked turbidity in the liquid. No precipitate should separate. The beaker containing the solution should be placed on a sheet of black paper so that the disappearance of the yellow cloudiness can be easily seen.

As copper acts in the same way that nickel does, it must be removed before the Ni is titrated. Small amounts of Mn do not seem to affect the titration; if much is present the liquid will grow turbid and make it difficult to see the end reaction. Hence with metals high in Mn it should be removed by using Na_2CO_3 in the neutralization, and then bromine as noted before.

That the results by this process may be satisfactory it is essential that the conditions be kept very uniform. The volume of the cyanide solution required for a given amount of nickel depends somewhat upon the excess of NH_4OH present, the amount of ammonium salts in the solution, the volume of the liquid, and the temperature. The solution must not be hot enough to feel warm to the hand.

Solutions Required: Standard KCN.—Dissolve 4 grams of pure KCN in 1 litre of water. One c.c. of this solution will equal approximately 0.001 gram of Ni.

Silver Nitrate Solution.—Dissolve 0.5 gram of $AgNO_3$ in 1 litre of water.

Potassium Iodide Solution.—Dissolve 20 grams of KI in 1 litre of water.

Standardize the cyanide solution against recrystallized ammonium nickel sulphate $(NH_4)_2Ni(SO_4)_2 6H_2O$, as follows: Prepare a solution of this salt 3.331 grams to the litre ; 50 c.c. of this will contain 0.025 gram nickel. Take 50 c.c. of this solution, dilute it to 100 c.c., and add approximately as much HCl as is present in the nickel solution from the steel. Add NH_4OH until the free acid is just neutralized, and then add 1 c.c. more. Now add 5 c.c. of the silver nitrate solution and 5 c c. of the potassium iodide solution. The liquid will become opalescent from the formation of AgI. Now set the beaker upon a sheet of black paper and run in the cyanide solution from a burette until the turbidity disappears. The volume used is that required for the nickel and the silver indicator. Now repeat the process, using 100 c.c. of water and leaving out the nickel solution, but putting in the HCl, NH_4OH, $AgNO_3$, and KI as before. The volume of cyanide used in this case will be that required for the AgI alone. Deduct this from that found in the first test and the difference is the volume of the cyanide solution required for 0.025 gram of nickel. From this calculate the value of 1 c. c. of the cyanide solution. As the cyanide solution does not keep its strength long, it must be restandardized frequently.

Titration of the Ni Solution from the Steel.—The volume of the solution should be 100 c. c. Add NH_4OH until the free HCl is neutralized and the liquid reacts neutral; then add 1 c. c. in excess. Add now 5 c. c. of the $AgNO_3$ and 5 c. c. of the KI solution and titrate with the cyanide as in standardizing. The number of c. c. used minus the volume of the KCN required for the AgI alone, multiplied by the value of 1 c. c. in nickel gives the amount of nickel in the steel.

Notes on Metallurgical Analysis.

The above processes for the determination of nickel in steel can be applied with slight modifications to other materials. If silicon is present in the metal it must be removed by evaporating the original solution to dryness, then taking it up in HCl and proceeding as directed, after concentrating the liquid to 10 c. c.

In analyzing ferro-nickel, dissolve 20 grams in aqua regia, evaporate the solution to dryness, take up in HCl, dilute to 1 litre and take 50 c. c. (equals 1 gram) for the analysis. Evaporate to 10 c.c. with HCl and proceed as usual.

Campbell. Jour. Am. Chem. Soc. 1894. p. 96.
Sargent. Jour. Am. Chem. Soc. 1899. p. 854.

THE DETERMINATION OF TUNGSTEN AND CHROMIUM IN STEEL.

When steel containing chromium and tungsten is dissolved in a mixture of HCl and HNO_3 the solution evaporated to dryness, and the residue treated with HCl the chromium goes into solution with the iron and manganese; while the tungsten is left insoluble as WoO_2 with the SiO_2^-. In order to render the WoO_2 entirely insoluble, more than one evaporation with HCl is necessary. When treated with H_2SO_4 and HFl, WoO_3 is not volatilized and can be thus freed from SiO_2. When a solution of chromium in concentrated HNO_3 is treated with $KClO_3$, as in the Ford-Williams method for manganese, the chromium is entirely oxidized to CrO_3 at the same time that any manganese present is precipitated as MnO_2. The MnO_2 can be filtered off on an asbestos filter while the whole of the chromium will be found in the filtrate. The following method is based on these reactions. It is essentially that published by A. G. McKenna, Proc. Eng. Soc. Western Pa. 16; 119.

PROCESS.

Dissolve 5 grams of the metal in HCl, using 60 c. c. of 1 : 1 acid. Add 10 c. c. of concentrated HNO_3 and evaporate to dryness. Take up the residue by digesting with 15 c. c. of concentrated HCl and again evaporate to dryness. Again take up in 20 c. c. of concentrated HCl, digesting without boiling until dissolved, dilute to 100 c. c. and boil. Filter from the $SiO_2 + WoO_3$. Wash thoroughly with 5 per cent. HNO_3 and ignite and weigh the residue of $WoO_3 + SiO_2$ in a platinum crucible. Now add a drop of H_2SO_4 to the residue in the crucible and then 4 c. c. of HFl. Evaporate off the acid under a good hood, then ignite and weigh. This residue is WoO_3. It should be of a lemon-yellow color. As it frequently contains a little ferric oxide, fuse it with 2 or 3 grams of Na_2CO_3 and dissolve the fusion in hot water. The sodium tungstate will all dissolve. If any Fe_2O_3 is left insoluble, filter it off, wash it thoroughly with water and ignite and weigh it. Deduct the amount from the weight of the impure WoO_3. Evaporate the fil-

trate from the $SiO_2 + WoO_3$ with 50 c.c. of concentrated HNO_3 to decompose the HCl. Dilute to 200 c.c. with concentrated HNO_3 and precipitate the Mn as in the Ford-Williams process, using 10 grams of $KClO_3$. After the MnO_2 is precipitated, continue the boiling until all the Cl is expelled. This will require concentrating at least one-half the volume. Filter off any MnO_2 onto asbestos as usual. It can be used for the determination of manganese. Cool the filtrate containing the chromium as CrO_3 and dilute it to 500 c. c. with cold water. The temperature of the liquid must now not be over 20° C. Now add a measured volume of a standard solution of ferrous sulphate and immediately titrate the excess over that oxidized by the CrO_3 with a standard solution of permanganate.

As one molecule of CrO_3 will oxidize three atoms of iron from the ferrous to the ferric state, the amount of chromium can be directly calculated from the difference between the ferrous iron in the solution added and that remaining unoxidized as shown by the titration.

Chromium : iron : : 52.1 : 168, or 0.31 times iron equals chromium.

If the "manganese standard" of the permanganate is known, it is only necessary to titrate the ferrous sulphate solution with it, and then deduct from the amount of the permanganate equal to the ferrous sulphate added, the amount taken in the titration of the chromium solution. This gives the volume of the solution equal to the chromium, and the Mn value of this multiplied by 0.631 will give the Cr.

The method may be somewhat shortened by using smaller amounts of sample and reducing the reagents proportionately. If no tungsten is present, simply proceed as in the Ford-Williams method for Mn, but be careful to boil out all the Cl. Then determine the Cr in the filtrate as above. According to Mahan, the HNO_3 solution containing the MnO_2 may be diluted with water and then cooled and filtered through paper instead of asbestos. It is then partly neutralized by NH_4OH and the Cr determined as above. The solution must be diluted to at least ten times its volume.

Mahan. Jour. Chem. Soc. 1900. p. 1057.

THE DETERMINATION OF ALUMINUM, COPPER AND ARSENIC IN STEEL AND IRON.

These elements occasionally occur in small amounts and may be determined by the following methods:

ALUMINUM.

Stead's Method. Jour. Soc. Chem. Ind. 1889. p. 965. This depends upon the complete precipitation of aluminum as phosphate in the presence of sodium phosphate in boiling solutions containing an excess of sodium thiosulphate. Acetic acid and acetates do not interfere. Iron in the ferric state must be absent. Ferrous iron does not interfere. The excess of thiosulphate rapidly reduces the ferric iron at a boiling heat.

Process.—Dissolve 11 or 22 grams of the metal, according to the percentage of Al, in 44 or 88 c. c. of concentrated HCl. Evaporate to dryness to separate SiO_2. Take up in HCl and filter. Dilute the filtrate to 200 c. c., add 3 c. c. of a saturated solution of Na_2HPO_4, then NH_4OH till a slight permanent precipitate appears. Dissolve this by adding HCl drop by drop. Heat to boiling and add 50 c. c. of a saturated solution of sodium thiosulphate. Now boil gently till all the SO_2 is expelled, which will usually take about half an hour. Filter off the precipitate rapidly, using a large filter, and wash it thoroughly with hot water. The precipitate consists of sulphur, aluminum phosphate and a little iron. Wash the precipitate back into the beaker. Let it settle and decant off the excess of water through the filter. To the remainder in the beaker, which should not exceed 5 or 6 c. c., add an equal volume of concentrated HCl and warm to nearly boiling, stirring it up thoroughly. Now filter the solution through the same filter into a platinum dish, washing filter and precipitate thoroughly. Evaporate this solution containing the aluminum phosphate to dryness. The residue on the filter is sulphur and may be

rejected. It is well to burn it, however, and examine any residue for aluminum. To the dry residue in the platinum dish add 2 grams of pure NaOH (from sodium) and 1 c. c. of water. Heat till the sodium hydrate dissolves, and then stir the residue thoroughly into it. Cool, add water and boil five minutes. Transfer the turbid solution to a flask and dilute to 110 c. c. Filter through a dry filter and collect 100 c. c. of the filtrate, equivalent to 10 or 20 grams of the steel, according to the amount taken. Neutralize with HCl in slight excess. Add 3 c.c. of Na_2HPO_4 solution and again precipitate by adding 10 c.c. sodium thiosulphate and boiling. After the precipitate is formed and the SO_2 expelled, add 2 or 3 c. c. of a saturated solution of ammonium acetate. Boil two minutes longer and filter. Wash with hot water till free from chlorine. Burn off, ignite, and weigh the $AlPO_4$, which contains 22.36 per cent. of aluminum. Run a blank on all the reagents used and make a correction for any Al_2O_3 or SiO_2 so found. If Cr is present, it will be in part precipitated with the aluminum. Its presence will be shown by the yellow color it gives to the soda fusion. It can be removed by adding a few drops of an alkaline sulphite to this solution and boiling for some time, the CrO_3 will be reduced and precipitated.

COPPER.

Dissolve 10 grams of the metal in 60 c. c. of concentrated HCl in a flask closed with a rubber valve or simply fitted as for the evolution method for sulphur, the delivery tube dipping into water. Boil the solution until most of the acid is driven off and crystals of $FeCl_2$ begin to separate. Now cautiously add 300 c. c. of warm water and heat till the iron salts are dissolved. Now pass a rapid current of washed H_2S through the liquid for ten minutes. Cork the flask and let the precipitate settle. Finally filter off rapidly through a 11 cm. ribbed filter, rinse out the flask and wash the filter and precipitate thoroughly with water containing a

little H_2S. The residue left on dissolving the iron may contain copper and must be treated with the precipitate. Now put the filter and its contents into a porcelain crucible and cautiously burn it off at a low heat. It is not necessary to burn out all the carbon provided the sulphur be oxidized. Empty the crucible into a small beaker. Rinse out the flask and crucible with 10 c. c. of hot HNO_3, sp. gr. 1.2 Add this to the burnt residue in the beaker. Digest at a boiling heat for some minutes till all action ceases. Dilute to 50 c. c., add NH_4OH till neutral, and then 3 c. c. in excess and filter. If much ferric hydroxide separates, redissolve it in 2 c. c. of HNO_3 and reprecipitate as before, combining the filtrates. In the blue liquid the Cu may be estimated by KCN (See Assay, of Copper Ores), or in the case of small percentages, colorometrically by comparing the depth of color of the solution with that obtained by adding the same excess of NH_4OH to a solution of copper nitrate containing a known amount of Cu and diluted to the same volume. One milligram of Cu is about as much as can be estimated in this way. If more is present, dilute the solution to a known volume and divide it.

ARSENIC.

This element may be estimated by dissolving 10 grams of the metal in HNO_3 sp. gr. 1.2, evaporating and baking as for phosphorus, dissolving the residue in concentrated HCl without heating, which might volatilize $AsCl_3$, diluting, reducing with Na_2SO_3 and precipitating the As by H_2S as As_2S_3. (See p. 47). The As_2S_3 is then oxidized by fuming HNO_3 and precipitated with magnesia mixture and weighed as $Mg_2As_2O_7$. For details, see Fresenius' Quantitative Analysis.

The following method is much shorter and is sufficiently accurate when only small percentages are present. It depends upon the volatilization of As as $AsCl_3$ when a solution containing it is boiled with HCl and a large excess of ferric and ferrous chloride. In order that the volatilization may be rapid and complete, the liquid should have its boiling point raised to about 108° C. by the addition of $ZnCl_2$ or $CaCl_2$, and should contain concentrated HCl.

Process.—Arrange the flask as for the evolution sulphur

method. The delivery tube must have a couple of good size bulbs in it to catch any $FeCl_3$ mechanically carried over. The test tube receiving the vapors should stand in a large beaker of cold water.

Dissolve 100 grams of commercial $FeCl_3$ in 150 c. c. of concentrated HCl in a 500 c. c. beaker. Gentle warming accelerates the solution. When dissolved, add cautiously 4 grams of pulverized zinc. When this is dissolved, boil the solution gently for ten minutes to expel the traces of As found in the reagents. With new chemicals it is well to do this boiling in the flask, as in the regular determination, and determine the As given off. If this is more than a trace, get other reagents. After boiling, cool the mixture. Weigh into the empty evolution flask 10 grams of the metal to be tested. Put 100 c. c. of cold water into the large test tube into which the delivery tube dips. Now add the $FeCl_3$ mixture through the funnel tube, running it in very cautiously to avoid violent action. It may take 8 to 10 minutes to do this. Warm if necessary until the iron is dissolved; then heat to boiling and boil steadily for 15 minutes. The As will practically all distill over as $AsCl_3$ and condense in the water in the test tube. The delivery tube should pass to the bottom of this tube and the water in the beaker in which the test tube is placed be kept cold; as the liquid in the tube must not be allowed to reach the boiling point. At the end of 15 minutes take out the test tube and substitute a second one containing a similar amount of water, and boil the solution ten minutes longer. The second tube should show no more than a trace of arsenic.

The liquid in the tube is poured into a beaker, and if not strongly acid made so by adding HCl, heated to near the boiling point and precipitated by a rapid current of H_2S. The As_2S_3 will separate promptly and may be filtered off onto a small weighed filter washed first with water, then twice with absolute alcohol, then with pure bisulphide of

carbon (to remove any free S). It is then dried at $100°$ C and weighed.

The As in the solution from the tube can also be estimated volumetrically with iodine. as follows: Cool the liquid and add a solution of Na_2CO_3 until the HCl is just neutralized; then add 1 c. c. in excess. Now add starch paste and titrate with iodine as in the sulphur method. As 2 of iodine are equivalent to 1 of $AsCl_3$, 1 atom of As is equivalent to 1 of sulphur: or by weight S : As : : 32 : 75. Hence, the sulphur value of the iodine taken multiplied by 75 and divided by 32 will give the amount of the arsenic present.

Gibb. Jour. Soc. Chem. Ind. 1901. p. 154.

Norris. Jour. Soc. Chem. Ind. 1902. p. 393.

THE ANALYSIS OF COAL AND COKE.

In the laboratory examination of coal the points to be investigated are usually: First, the amount of moisture that it contains as it occurs in the mine or on the market. Second, the amount of the impurities present that affect its use, such as ash, sulphur, and phosphorus. Third, the amount and quality of the coke that it will produce. Fourth, the improvement that it undergoes by "washing." Fifth, the fuel value, including the calorific power and the evaporating power.

The sampling of coal is always a matter of considerable difficulty, as it deals with a mechanical mixture of several minerals which differ greatly in specific gravity; namely, pure coal, slate, bone coal and iron pyrites. These constituent minerals may occur in all degrees of size; for instance, the pyrites may be present as barely visible grains scattered all through the coal or as large lumps and streaks. It is obvious that in the latter case the difficulty is formidable of securing a small sample which shall contain the same percentage of the heavy pyrites as does the mass from which it is drawn.

Finely crushed coal is liable to oxidation and change of composition on standing exposed to air at ordinary temperatures. Hence the analysis should be made soon after the final sampling.

It is impossible to give directions for sampling applicable to all cases, but in addition to the general precaution stated in the paragraph on Sampling on page 14, two or three special points may be emphasized. First, the sample must be large, at least 150 or 200 lbs., and if the ingredients are very coarse, still larger. Second, every care must be taken to make the sample impartial. Third, no separation of the sample by gravity must occur; as, for example, by jerking of a portion from the end of a shovel full of coal, a procedure which will always give an undue amount of coarse and light material. Fourth, the sample must be reduced as promptly as possible. It may be quartered down to fifteen or twenty pounds at nut size. This should be crushed to quarter-inch and then "quartered" down to a sample that can be kept in a sealed fruit jar. Samples that are too wet to crush to quarter-inch size should be weighed in bulk, spread out and allowed to air dry till they can be handled, again weighed, and the sampling completed, of course calculating the subsequent analysis back to the original coal.

The laboratory processes in use for coal testing comprise the

proximate analysis. the ultimate analysis, the determination of sulphur and phosphorus, tests of the coking power, washing the coal, and finally the determination of the heating power either by calculation from the results of the ultimate analysis or by use of the calorimeter.

THE PROXIMATE ANALYSIS OF COAL.

This is the one most usually made. The process is conventional and must be strictly followed, as any departure will lead to much variation in results on moisture, fixed carbon, and volatile matter. The method which follows is that reported by the Committee on Coal Analysis of the American Chemical Society.

See Jour. Am. Chem. Soc. 1899. pp. 1116, 1145.

The Determination of the Moisture and Ash.—Weigh 1 gram of the coal into a porcelain or platinum crucible. Put the crucible, uncovered, into a drying oven and keep it at 104° to 107° C for exactly one hour. Cool and weigh. The loss in weight is called moisture and represents with sufficient exactness the hygroscopic water in the coal. Drying for a definite time instead of to constant weight is necessary ; as coal begins to gain weight by oxidation before all the moisture is expelled. Now set the crucible over a low flame, inclined so that the air can circulate in it. Set the cover up against the front of the crucible to help the draft. After the volatile matter has burned out, the flame may be turned up a little ; but strong heating at first will greatly delay the subsequent combustion of the carbon. The burning can sometimes be hastened by cautiously stirring the material with a fine platinum wire. When all the carbon appears to have been burned, cool the crucible and weigh it. Then replace it over the burner and heat for at least ten minutes longer. Cool and weigh again, continuing this until two consecutive weights agree. It is essential that the ash be burned to constant weight; as it will often continue to lose weight after all visible carbon has disappeared. From the final weight subtract the weight of the crucible to get the weight of the ash.

Where many analyses have to be made, a small muffle furnace is very convenient for burning coal to ash. The coal can be burned in porcelain crucibles and then the ash brushed out into a watch glass and weighed with practically no error, if care is taken to burn the coal long enough to insure complete combustion. The muffle can be heated by gasolene or gas.

See Stoeck. Jour. Soc. Chem. Ind. 1897. p. 304.

The Determination of the Volatile Combustible Matter.—Weigh 1 gram of the sample into a platinum crucible of 25 to 30 c.c. capacity. The crucible must have a closely fitting cover. Set the covered crucible over a large Bunsen burner and heat for exactly seven minutes. Remove the burner let the crucible cool, and weigh it. Do not uncover the crucible till nearly cool. The upper surface of the cover should burn clean, but the under surface should be covered with carbon. The burner should give a flame 20 centimeters high when burning free, and the crucible should be so placed that the bottom will stand from 6 to 8 centimeters above the top of the burner, and should be supported upon a platinum wire triangle. The process must be conducted where the flame will not be disturbed by drafts. Variation in any of these details will affect the results. It is well to select one burner and always use it for this work.

The loss in weight less the percentage of moisture gives the volatile combustible matter. The weight of the residue in the crucible gives the coke, and the weight of the coke minus the weight of the ash is reported as the "fixed carbon" in the coal.

Of course the sum of the percentage of moisture, volatile combustible matter, fixed carbon, and ash will be 100.

The method recommended by the Committee differs slightly from the one used by the writer for the coal analyses for the Ohio Geological Survey, which followed much more closely the original method of Heinrichs (Chem. News. Vol. xvii. p. 53).

In the older method, after determining the moisture in the coal as directed, the crucible containing the same portion of coal is heated for three minutes over the Bunsen burner and then three and

a half minutes over the blast lamp, and the further loss called volatile combustible matter. The same portion was then burned to ash. The writer has analyzed a number of samples by both methods with but little difference in the results. The burning out of the ash is more rapid where the coal has not been previously coked by exposure to a high temperature.

The determination of Sulphur in Coal—Eschka's Method.— Sulphur exists in coal in three forms: Pyrites, "organic sulphur," and sulphates. By heating coal with a mixture of MgO and Na_2CO_3, and with ample access of air, all unoxidized sulphur is converted to sulphites and sulphates of soda and magnesia. On boiling the burned mass with water, these, as well as any sulphuric acid existing previously in the coal as sulphate, are all dissolved out as alkaline salts. By adding bromine water to the solution the sulphites are oxidized to sulphates, and then the total sulphur can be estimated as $BaSO_4$, by precipitation with $BaCl_2$.

Preparation of the Soda Magnesia Mixture (Eschka Mixture).—Procure a "light" calcined magnesium oxide, which must be free from sulphur and water. If it contains moisture, ignite it at a dull red heat in a covered platinum crucible. The heavy dense oxide is not satisfactory.

Mix two parts of the MgO with one part by weight of pure Na_2CO_3 previously dried at a dull red heat. Grind the two together till thoroughly mixed, and keep the mixture in a glass stoppered bott'.

If a satisfactory sample of sulphur-free MgO is not available, it may be prepared as follows:

Take a good quality of commercial "light calcined magnesia;" add about two per cent. of c. p. sodium carbonate, and then stir it up in enough boiling water to make a thin liquid. Boil the mixture a few minutes and let settle; decant off the liquid by a siphon. Add water, stir up, settle, and again decant. Continue this washing by decantation until a portion of the liquid, after being acidified with HCl, shows no trace of sulphates when tested with $BaCl_2$. Now

pour the MgO onto a large filter, let it drain and air dry.   It is now free from sulphur compounds.

Ignite the air dry MgO in a covered platinum crucible until all water is expelled.

A clean tin bucket can be used in this process where a quantity is to be prepared.

Process.—Weigh one gram of the coal or coke (which must be finely powdered, especially in the case of coke), then weigh or measure out roughly two grams of the "Eschka Mixture." Put about two-thirds of this into a 30 c.c. platinum crucible. Add the weighed coal and stir the mixture in the crucible thoroughly with a small platinum spatula or glass rod, and then settle it down by tapping the crucible on the table. Now cover the contents of the crucible with the remaining portion of the "Eschka Mixture." Set the crucible in an inclined position, over a small *alcohol* flame, so that the tip of the flame may barely touch the crucible near the *top of the mixture.* The heat must be carefully regulated, so that no blackening of the white cover layer takes place, and no trace of smoke appears.   The cover should be laid against the mouth of the crucible to assist the draught. The mixture soon ignites and will gradually burn through, as may be observed through fissures which open in the mass. The coal will usually burn completely in less than an hour. The heat may be raised toward the end of the combustion and the lamp set back under the bottom of the crucible. A higher heat may be used with cokes from the start; as these give no volatile products and burn slowly. Stir up the powder occasionally with a hot glass rod or platinum wire. When the burning is complete, all trace of the black coal will have disappeared and only a light, reddish gray mass remain. Cool and then pour the powder into a 200 c.c. beaker. Add about 75 c.c. of boiling water, stir and digest on a water bath. Then filter, washing the residue twice by adding about 30 c.c. of hot water, and decanting off, then transfer to the filter.

Wash on the filter until the volume of the filtrate amounts to about 200 c.c. This will extract practically all of the sulphur.

Add bromine water to the filtrate till the liquid is colored yellow; then add 3 c.c. of HCl and warm till the CO_2 is expelled. Test the solution with litmus paper to make sure that it is distinctly acid. Then add 10 c.c. of $BaCl_2$ solution (10 per cent.). Set the beaker on a warm plate, but do not let it come to boiling. Stir the liquid occasionally until the $BaSO_4$ becomes granular and settles well. Now filter, wash, dry, ignite, and weigh the $BaSO_4$. Calculate the sulphur as S.

Always examine the *residue* which was extracted with water, by washing it off the filter into a beaker, and then adding a little HCl and warming. All will dissolve but a little ash. If more than a trace of *unburned* coal is seen in the residue, the analysis must be repeated.

The residue sometimes retains a very small trace of sulphur. To test it, add a little bromine water with the HCl as above and boil. Filter off the liquid and add $BaCl_2$. If any sulphur is found, add it to the main precipitate.

This is by far the best method for the determination of sulphur in coals. If care be taken in all details, especially as to rate of heating, there is no loss of sulphur whatever.

It has been proposed to substitute K_2CO_3 for the Na_2CO_3, the claim being made that there is less danger of loss of S with the potassium carbonate, but the writer's experience has shown it to be absolutely unnecessary.

The use of *alcohol* instead of gas as a source of heat is *essential*. All coal gas contains sufficient sulphur to *vitiate* the results.

The most difficult step in the process is the burning out. In analyzing coke much time can be saved by using a higher heat than is given by an alcohol lamp. This can be obtained by using a gasolene blast lamp or working in a muffle heated by gasolene. If the muffle is heated by coke or coal gas, care must be taken that no sulphur gets into it from the fuel.

Determinations of ash in coal and coke must not be made in the muffle at the same time with sulphur determinations; as the SO_2

formed will be absorbed by the "Eschka Mixture" and make the results high.

Cokes can be burned with "Eschka Mixture" in a platinum dish. They should be stirred frequently, which will hasten the combustion. It is unsafe to treat coals high in volatile matter in this way; because the gas given off must be burned in the mixture and not on the surface, or sulphur may escape. They must be burned in the crucible, and by properly regulating the air supply and the temperature the gas can be rapidly burned as it is given off. When the volatile matter is expelled the heat can be raised and the mixture stirred.

A blank determination must be run on the reagents.

Eschka. Zeits. Anal. Chem. vol. XIII. p. 344.
Drown. Trans. Am. Inst. Min. Engs. vol. IX. p. 660.

The Determination of Phosphorus in Coal and Coke.—10 grams of the coal are carefully burned to ash in a porcelain crucible. The ash is then analyzed for phosphorus exactly as though it were an iron ore, excepting that it is always necessary to fuse the insoluble portion. HCl will not dissolve all the P out of the ash even on prolonged boiling, though the amount left is usually very trifling.

Process.—Mix the ash from 10 grams of the coal with six times its weight of pure Na_2CO_3 and half its weight of $NaNO_3$. Fuse the mixture in a platinum crucible, soften up the fusion with water, dissolve in an excess of HCl, evaporate to dryness, take up with HCl and water, and filter from the SiO_2; then proceed as by the yellow precipitate method for phosphorus in iron ores (p. 51).

The fusion can be avoided by the use of hydrofluoric acid as follows: Add 5 c.c. of dilute HCl and 10 c.c. of HFl to the ash in the platinum crucible. Evaporate to dryness in a good hood; do not bake the residue and thus render it insoluble. When cool, add 15 c.c. of dilute HCl and heat. The residue should dissolve completely, but a little insoluble matter may be filtered off and neglected. Put the solution into a flask, add NH_4OH, then HNO_3, then molybdic acid solution, and "shake down" the phosphorus as in the Emmerton method. The yellow precipitate may be either weighed or titrated.

See J. M. Camp. Iron Age, 65, p. 17. Also "Methods Around Pittsburgh," p. 139.

THE ULTIMATE ANALYSIS OF COAL.

The Determination of the Carbon and Hydrogen by Combustion in Oxygen.—

The coal, placed in a boat of porcelain or platinum, is burned in a combustion tube, through which a current of purified air and oxygen gas is passed. The H_2O and CO_2 produced are absorbed and weighed. As the coal contains sulphur, the gases produced by the combustion must be passed over lead chromate to absorb the SO_2 formed.

The same chromate can be used for many determinations. As long as it does not turn green for more than one-fifth of the length in the tube it is perfectly safe. The writer has used the same chromate for over fifty combustions, and then tested it by burning sulphur in the tube, and found no SO_2 escaping the chromate.

The principal difficulty in the process arises from the fact that coal begins to decompose at a low temperature, giving off among other products methane, a gas which it is very difficult to burn completely, and which is very likely to escape from the combustion tube unoxidized. To secure its complete combustion a *long* and *hot* layer of copper oxide is necessary.

The process requires close attention to details and skill in fitting up and manipulating apparatus. The precautions mentioned under the combustion method for carbon apply equally here, especially as to the purity of the oxygen and the copper oxide. The latter should be examined for $CaCO_3$ or other carbonates which are liable to give up CO_2 on heating, and also for bases which may absorb CO_2. $CaCO_3$ will be decomposed at one temperature, and the CaO formed will absorb CO_2 at another. CuO can be examined for CaO by extracting it with a little dilute HNO_3, adding NH_4OH in excess, and then testing the liquid with $(NH_4)C_2O_4$. The "wire" oxide is the best and should be used.

The asbestos used in the tube must be freed from carbonates by treatment with HCl and ignition, as directed on p. 127.

The oxygen must be tested as to its purity, and must not be kept in rubber bags or passed through long rubber tubes.

Oxygen can be purchased in cylinders, or it can be made by heating a mixture of pure $KClO_3$ with one-third of its weight of MnO_2, in a 250 c.c. round bottomed, long necked flask of hard glass (Kjeldahl flask). The flask should be surrounded by a cylinder of wire gauze to protect the face in case of an explosion. The mixture must be tested for carbon by first heating a little of it on a platinum crucible cover; it should not sparkle or flash. The gas so made will contain some Cl and CO_2 which must be removed by KOH solution.

The Arrangement of the Apparatus.—This is in many respects similar to that used in the determination of the carbon in iron, except that as the water is to be weighed as well as the CO_2, tubes for absorbing it are added.

The train comprises: First, a gas holder for the oxygen. The one described on p. 125 is very satisfactory. About 500 c.c. of oxygen is required for each combustion.

Where only an occasional combustion is made a simple gas holder can be made of a couple of glass bottles. Such an arrangement is shown in Fig. 8, p. 126

Second, the purifying train for the air and oxygen. This is made in duplicate, as described under the determination of carbon, and includes in addition to the reagents there given a bottle containing sulphuric acid to absorb the traces of ammonia or its salts usually present in the air of a laboratory. If these were not taken out they would burn in the tube and form water and make the results on hydrogen too high. As it is as important to purify the air from moisture as from CO_2 in this process the train is made larger and separate U tubes are used for the soda lime and the $CaCl_2$.
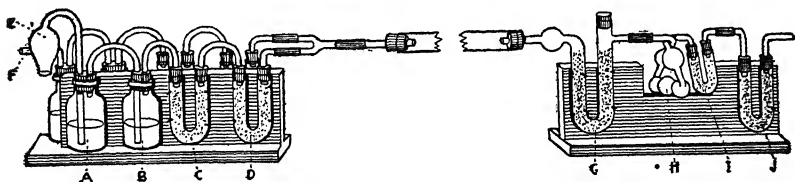
FIG. 9—Purifying and Absorbing Train for Coal Combustions.

Fig. 9 shows the details: A is a bottle with moderately concentrated H_2SO_4; B is a bottle with about 50 c.c. of KOH solution of 1.27 sp. gr.; C is the U tube with the soda lime, and D is the U tube with the $CaCl_2$.

Third, the combustion tube: This should rest on asbestos in the trough of a long gas combustion furnace. The tube should be made of the best infusible glass and have an internal diameter of about half an inch. The walls

of the tube must not be too thick or they will crack.   The ends of the tube should be rounded by heating and should be fitted with good soft corks, well rolled.   Rubber connections with this tube are not to be recommended, as they become warm and are liable to give off hydrocarbon vapor and to absorb some CO_2.   A long tube and furnace are necessary.   The writer uses a furnace with twenty-five burners and a tube forty inches long.

The tube is filled as follows: A space of five to five and one-half inches is left empty at the end nearest the absorbing train.   Then follows: 1. A plug of asbestos. 2. Five inches of fused $PbCrO_4$ in small lumps. 3. An asbestos plug. 4. Twelve to fourteen inches of pure, recently ignited "wire" CuO (or a close coil of fine copper gauze thoroughly oxidized by heating it in a stream of pure oxygen). 5. An asbestos plug. 6. The "boat" for holding the coal.   There must be thirteen or fourteen inches of empty tube following the last asbestos plug, so that the part of the tube in which the "boat" is placed will be well in the furnace, and yet the tube itself project at least four inches outside of the furnace.   The end of the tube is connected by a cork, glass tube, and rubber connection with the purifying train.   The cork connections in the ends of the combustion tube must not become hot enough to run any risk of being burned; hence a sufficient length of tube must project from the furnace at each end.   These projecting ends should be further protected from the heat of the furnace by discs of sheet asbestos six or seven inches in diameter, with holes in the center through which the combustion tube passes.

With a tube arranged as above it is not necessary to insert a copper coil behind the "boat," as is sometimes directed, provided the coal is slowly heated so as to expel the volatile matter gradually, and that a continuous current of air or oxygen is kept passing through the tube, so as to prevent the products of the decomposition from working back, condensing in the cool part of the tube, and so escaping combustion.

Fourth is the absorbing train following the combustion tube, shown in Fig. 9, and consisting of G, a $CaCl_2$ tube, the end of which is inserted into the cork of the combustion tube; H, Liebig potash bulbs; I, a soda lime, $CaCl_2$ tube similar to that used in connection with the potash bulbs in the determination of carbon in iron; J, a guard tube similar to I but reversed, which is connected with an aspirator for drawing air through the apparatus.

A "Mariotte bottle," arranged as shown in Fig. 10, makes the best aspirator. The suction tube, A, passes in through a rubber stopper at the top and reaches nearly to the level of the run-out tube. By slipping the suction tube up or down, the suction head can be regulated so as just to overcome the resistance of the train, and will then remain exactly the same as long as the water in the bottle is above the end of the tube, and thus the rate of aspiration can be more easily kept constant.

Fig. 10.—Mariotte Bottle Aspirator.

Testing the Apparatus.—*First*, see that it is *perfectly tight* by starting the aspirator and shutting of the entrance of air. *Second*, heat the tube redhot throughout and aspirate two litres. Detach and weigh the potash bulbs and U tube. Connect up again and aspirate one-half litre of oxygen and then two litres of air. Detach the tubes and weigh. There should be neither gain nor loss of weight. When consecutive weighings are found to agree within 0.5 milligram, the apparatus is ready for the analysis.

Process of Analysis.—Ignite and cool the boat. Weigh into it 0.2 gram of the finely pulverized and well mixed coal. (The sample must be made *very fine*, or weighing so small a quantity average results will not be obtained.) Insert the boat into its proper place and connect up the apparatus. Then carefully heat the $PbCrO_4$ to *dull* redness and the CuO to bright redness, drawing a slow current of air through the apparatus all the time. Now heat the tube

behind the coal and then the coal itself, cautiously, until the volatile products are slowly driven off and carried forward over the hot CuO. Then introduce oxygen, regulating the supply so as to avoid too vigorous combustion and consequent fusion of the ash, which will lead to retention of carbon. After the carbon is all burned, which is shown by the sudden disappearance of the glow, continue the oxygen for two minutes, then cut it off and aspirate air. Turn off the gas burners and let the tube cool. Continue the aspiration until 1200 c.c, or more (at least seven times the capacity of the tube and absorbing train) has been drawn through. Now detach the absorption train and weigh. The increase in the weight of the $CaCl_2$ tube gives the water produced. This divided by nine gives the weight of the hydrogen in the coal. The increase in the CO_2 apparatus is the CO_2 ; $\frac{3}{11}$ of this is the carbon. The apparatus is now ready for another determination, as the CuO will all have been reoxidized by the air current.

The aspiration should be so regulated that not more than two or three bubbles pass through the potash bulbs per second. During the combustion in the oxygen the gas will consist largely of CO_2 and will be almost wholly absorbed, though the flow of oxygen into the apparatus may be quite rapid at the time. Care must be taken that the oxygen supply is sufficient to prevent back suction at this time.

As soon as the CO_2 is absorbed the gas may begin to run through the potash bulbs too rapidly unless the gas supply is promptly reduced.

The pressure of the gas in the tube should be kept near that of the atmosphere. This can be accomplished by careful regulation of the gas and the aspirator.

As was noted in the determination of carbon in steel, it is desirable to reduce the necessary aspiration to as small a volume as possible by using small connection tubes and a compact train. This both saves time and increases accuracy.

After the boat containing the ash is withdrawn from the tube, weigh it. The ash so determined should agree with that found in the proximate analysis.

The tube should be kept carefully closed with good corks when not in use. A train and tube such as that described can be used for months. A good tube of Jena glass, while it may twist out of shape badly, will not crack or blow if carefully handled. Fifty or more determinations can usually be made on one filling of the tube.

THE DETERMINATION OF THE NITROGEN IN COAL.

One gram of the very finely pulverized coal is boiled with 30 c.c. of concentrated H_2SO_4 and 0.5 gram of metallic mercury until the carbon is completely oxidized and the liquid is nearly colorless. A little potassium permanganate is then added. When the liquid is cool it is largely diluted with water, the mercury precipitated by K_2S, and the ammonia it contains determined by distillation after adding an excess of solution of NaOH. This is the "Kjeldahl process," and depends on the fact that all the nitrogen is converted into ammonia by the treatment with H_2SO_4. For a complete description of the process, see Report of the Proceedings of the Association of Official Agricultural Chemists: Bulletin of the U. S. Department of Agriculture, 1895, No. 46. The results on coal are accurate, provided the sample is very finely pulverized and time enough given in the digestion to entirely oxidize the coal. This may take two or three hours.

The soda-lime method can also be used and will give satisfactory results, provided the coal is completely burned and the soda-lime heated in the tube until it shows no more black color and leaves no unburned carbon when tested by solution in HCl. For a description of this method, see Fresenius' Quantitative Analysis.

THE OXYGEN IN COAL.

As no good method is known for the direct determination of the oxygen in coal, it is always determined by difference, the sum of the percentages of H, C, N, S, and ash being subtracted from 100 and the remainder called oxygen. The result so obtained is always inaccurate, the error increasing with the percentages of the ash and the sulphur. The weight of the ash does not represent that of the mineral matter in the coal, the pyrite in the coal being burned to Fe_2O_3 and the sulphur passing off as SO_2. Thus 4 of S in $2FeS_2$ is replaced by 3 of O in the Fe_2O_3, and the loss of weight is equal to $\frac{1}{4}$ of the S. For this reason many chemists use $\frac{5}{8}$ S instead of S in the determination of O by difference. As coals contain sulphur in other forms than FeS_2, and also frequently other compounds that lose weight on burning, such as $FeCO_3$ and $CaCO_3$, it is doubtful whether the results obtained in this way are any better than those given by the simple formula first given.

TESTING THE COKING POWER OF COAL.

The surest way to ascertain the quality of coke furnished by a coal is to test it in a regular oven; but as this involves considerable expense and a large quantity of coal, a laboratory test which would enable the chemist to form from a small sample, such, for instance, as can be obtained in prospecting by drill holes, a reasonably accurate idea of the cementing property of the coal, is very desirable.

Tests made by putting a box or barrel of the coal to be tested into an oven with other coal are misleading; as the gases in the oven carry carbon into the specimen tested, and will often give the appearance of a good coke to the product from coals of very inferior coking quality. The following method has been used by the writer for some years, and has proved generally useful. It consists in mixing the coal with a weighed amount of standard ground silica, coking the mixture in a small rectangular mould of platinum, and then testing the transverse strength of the little bar of coke so obtained. The apparatus consists of a small platinum "boat" two inches long, one-quarter inch deep, and the same width at the bottom, but having the sides flaring a little, so that the coke bar will readily drop out. The boat is provided with a close fitting cover, which overlaps like a box lid. The coal must be pulverized fine enough to go through an 80-mesh sieve.

Five grams of the powdered coal are thoroughly mixed in a small porcelain mortar with ten grams of ground silica. The platinum mould is then filled with the mixture, tapped to settle it, "struck even," and the cover put on. It is then set on a platinum support and heated over a good Bunsen burner till all flaming ceases and it is red-hot throughout. It is then cooled down to below redness, uncovered, and the block of the coke dropped out into water. Treated in this way, the dry, non-coking coals will fall to powder, but the coking coals form a more or less solid bar of coke two inches long and one-fourth inch square. If the bar is cracked or defective, it is rejected and a new one made. It is easy in a few moments to prepare in this way two or three sound bars.

These are then tested by laying them on two round wires one and one-half inches apart, and hanging a small wire loop over the middle of the bar. This loop carries a little bucket, into which small shot or "test lead" is carefully poured until the bar breaks. The bucket with its contents is then weighed and gives the breaking strength of the little bar of coke. Several tests should be made. They will vary considerably among themselves, but the averages are fairly reliable. Similar tests are made on several representative coking coals. By comparing the figures obtained from these coals

with that obtained from the coal to be tested, it can be ranked pretty accurately on a comparative basis. The writer uses for comparison, first, Connellsville coal; second, Allegheny County Pittsburg coal; and third, Pocahontas coal.

In order to determine the analysis of the coke produced from a coal, it is necessary to prepare a sample of the coke. This can be done in a small wind furnace as follows: Select two clay crucibles of such a size that one will set easily inside of the other. The writer uses a Denver fire clay " 20 gram assay " crucible for the inner and a large " Hessian " for the outer. Grind a cover onto the inner one with sand till it fits closely. Put the larger one in the furnace and let it get bright red hot. Meanwhile charge the smaller with 100 grams of the coal, crushed to about one-fourth inch mesh. Cover the smaller crucible and set it in the large one, throw a little coal in on top of it, and then carefully cover the larger one. At the end of an hour take out both, put a little more coal into the outer crucible, and then let them cool covered. When cool, take out the inner crucible and remove the coke from it. The object of the coal in the outer crucible is to prevent oxygen getting into the coke and burning out sulphur.

THE DETERMINATION OF THE POROSITY OF COKE.

The value of coke as a blast furnace fuel depends somewhat on its porosity, as its speed of combustion will increase with the surface exposed to the blast.

The porosity is usually expressed as the percentage that the volume of the pores forms of the volume of the coke.

It can be determined by weighing the coke in air and then in water, and then filling the pores with water and weighing it again.

The difficulty of filling the pores with water is, however, so great that the results are very uncertain. It requires long boiling in water and repeated exhaustions under an air pump to remove the air; and as there are probably pores that do not open to the surface, the filling is never complete.

The following method, depending on the determination of the true specific gravity of the coke substance and the measurement of the volume of the coke, is much preferable. It is essentially that published by W. C. Anderson, Jour. Soc. Chem. Ind.: Vol. XV. p. 20.

Determination of the Specific Gravity of the Coke Substance.—Into the neck of a 50 c.c. specific gravity bottle put a glass tube wide enough to fit air tight when surrounded with a collar made of a rubber tube. The glass tube must have a bulb about an inch in

diameter blown in it just above the bottle. It serves to catch any-thing boiling out of the flask and return it. Weigh into this bottle 3.5 grams of the pulverized coke. The coke must be ground in a Wedgewood mortar until it will go through a 40-mesh sieve, and dried at 100 ° C.

Now add about 20 c.c. of water to the bottle and set it on a water bath for fifteen minutes, shaking it occasionally till the coke powder is saturated. Now attach to the tube a Bunsen suction pump giving a good vacuum and exhaust the air till the liquid boils gently. Continue the boiling in a vacuum for two and one-half hours. Remove the flask, cool it, fill it up with water, and weigh as usual after inserting the stopper.

The bottle should have a counterpoise, of course, so that the weight obtained will be that of the coke and the water only. As the bottle holds exactly 50 grams of water, the specific gravity of the coke will be:

$$\frac{W}{W-(W'-50)}$$

in which W equals the weight of the coke, and W' the weight of the coke and water together. The true specific gravity of coke taken in this way varies from 1.75 to 2.00.

The Determination of the Volume or Apparent Specific Gravity of the Coke in Lumps.—Several average lumps should be selected and broken up just enough so as not to include any large mechanical fissures or cavities. They should then be brushed free from all dust and dirt and carefully dried and weighed. The volume of these fragments is then determined by measuring the amount of water they displace.

This can be done with sufficient accuracy in the following simple apparatus: Take a pint "ointment jar" with a wide mouth and a brass or aluminum screw cap. Cut a gasket of sheet rubber to fit over the end of the jar, so that the top will screw down onto it and make a tight joint. The end of the jar should be ground smooth. Cut a small hole in the top which should be just large enough to admit the stem of a 50 c. c. pipette. Screw on the top and fill the jar with water till it runs out of the top and includes no air bubbles. Carefully take out 50 or 100 c.c. of the water by means of a pipette put in through the hole in the top. Now unscrew the top, put in 50 or 100 grams of the weighed lumps of coke, shake them around to loosen air bubbles, replace the cap on the jar and run in water from a burette until the water comes exactly to the level of the hole. The difference between that measured out with the

pipette and that measured back in with the burette, will be the volume of the coke in cubic centimeters.

To find the volume of the pores in the coke, subtract its weight divided by its true specific gravity from the volume of the coke as determined above. The percentage that the pores form of the total volume of the coke will be:

$$100 \left(1 - \frac{\text{Wt. of the coke}}{\text{Vol. of coke} \times \text{Sp. Gr.}} \right)$$

TESTING THE EFFECT OF "WASHING" ON COAL.

The object of the washing of coal on jigs or other washers is the reduction of the ash and the sulphur in the coal. The benefit that a given coal will receive in the process will depend upon the form in which these impurities occur in it. Only the ash that is due to intermixed slate and the sulphur that is in the form of free pyrites can be removed by the process, which depends upon the difference in the specific gravity between these materials and the coal. The fineness to which the coal must be crushed in order to effect a satisfactory breaking apart of the heavy and light material will depend upon the nature of the coal seam. The finer the coal has to be crushed the greater will be the loss of coal in the slimes. All these points can be investigated in the laboratory.

The operation consists in crushing the coal to some determined maximum size, then separating it into a series of sizes by sieves, and finally separating these sizes into their heavy and light components.

The specific gravity of coal is less than 1.35, while that of the impurities is always above this figure; hence the separation into light and heavy parts can be made, as suggested by Dr. Drown, by mixing the coal with a solution of $CaCl_2$, of 1.35, sp. gr. on which the coal will float and in which the impurities will sink.

The apparatus needed consists of, first, a set of sieves of one-half, one-fourth, and one-twentieth inch mesh; second, a "miner's pan" or some equivalent in which a small quantity of material can be washed; third, a solution of calcium chloride of 1.35 sp. gr., made by dissolving one pound of crude $CaCl_2$ in a quart of water, and when the solution has cooled, diluting it to exactly the right gravity.

The coal is crushed, avoiding the production of dust as far as possible, until it will all pass through the half-inch sieve. The sample is then thoroughly mixed and a weighed amount of it (from three to five kilograms) sifted over the quarter-inch and the twentieth inch sieves. This divides it up into sizes $\frac{1}{2}$ to $\frac{1}{4}$, $\frac{1}{4}$ to $\frac{1}{20}$, and

$\frac{1}{5}$ to dust. The quantity in each size is then weighed and expressed in percentages of the whole. The two larger sizes are now separated in the chloride of calcium solution as follows: A beaker holding about a litre is nearly filled with the solution, the coal put into it a little at a time and well stirred to thoroughly wet it and detach all air bubbles. The coal rises to the surface, while the slate and pyrites settle to the bottom. Enough of the coal should be put in at a time to make a layer about an inch thick when it rises to the top. This is now skimmed out with a little dish or a dipper and dropped into a large funnel. the neck of which is closed with a small perforated porcelain disc. More coal is now added to the solution and the operation continued until all of the given size is thus separated. The coal in the funnel is then thoroughly cleaned from chloride of calcium by pouring water over it, allowed to drain. then spread out on paper, air dried and weighed. The chloride of calcium solution is then carefully poured off from the heavy material in the beaker, which is then washed out, dried and weighed. The material finer than one-twentieth of an inch is washed in the miner's pan. The coal is stirred up in water in the pan, and then by rocking the pan carefully the lighter portion is floated off and can be caught in a large dish where it is allowed te settle. The water is decanted off and the material air dried and weighed. The slate and pyrites left in the pan are also collected and dried and weighed. Each of the above products should then be analyzed for ash and sulphur. As a check, the analysis of the original coal should be computed from the analyses of these products, and should agree very closely with that of the original sample. The lighter products from the pan may be stirred up in water, and the portions settling in about one minute separately weighed. The fine stuff floating off is determined by difference, and will constitute approximately the coal lost in washing.

A little practice is necessary in order to properly manipulate the pan; but the treatment of the fine stuff in the $CaCl_2$ solution is very unsatisfactory, and as it forms only a small portion of the whole, inaccuracies in the panning will have little effect. From a comparison of the results shown on the various sizes, it may be desirable to repeat the experiment, crushing the whole of the coal to one-fourth inch or even to one-eighth inch, in order to separate very finely disseminated pyrites and secure a coal low in sulphur. But as the loss in washing falls almost wholly on the finer coal, the increase of the proportion passing the smallest sieve must be carefully noted.

If the coal is crushed to smaller sizes and then separated in the solution, all the finest dust must be first sifted out on a 60 or 80

mesh sieve, or it will clog up the filters and prevent the draining off of the solution. The dust can then be panned as usual.

See Drown. Trans. Am. Inst. Min. Engs. Vol. XIII. p. 341
Stoek. Jour. Soc. Chem. Ind. 1897. p. 304.

THE DETERMINATION OF THE HEATING POWER OF COAL.

By the heating power of a fuel is meant the total amount of heat produced by the complete combustion of the unit weight of the fuel.

In order to simplify calculations in technical work it is convenient to define the unit of heat as the heat required to raise the unit weight of water the unit of temperature. If the unit of weight is the kilogram and the unit of temperature the degree Centigrade, the unit of heat is the Calorie. If the units are the pound and the degree Fahrenheit, the heat unit is the British thermal unit.

With the heat unit defined as above, the number expressing the heating value of a fuel will be the same, whatever the unit of weight adopted, as long as the unit of temperature is unchanged. If the unit of temperature is changed, as, for instance, from Centigrade to Fahrenheit, the figure for the heating value will simply have to be changed in the inverse ratio of the dimensions of the units.

In the example quoted, as the ratio of the degree C to the degree F is $\frac{180}{100}$, heating powers in calories can be converted into heating powers in B. T. U. by multiplying them by $\frac{180}{100}$, or $\frac{9}{5}$.

The heating power of coke, anthracite and bituminous coal can be calculated with sufficient accuracy for many purposes from the ultimate analysis by Dulong's formula, as follows:

Heating power $= 8080\,C + 34460\,(H - \tfrac{1}{8}O) + 2250\,S.$

On the fuels specified the results by this formula rarely differ more than 2 per cent. from those obtained with the calorimeter.

Where accurate determination of the heating value is required, the direct combustion in the bomb calorimeter should be made.

For a description of the several forms of this instrument, the methods of using them, and the precautions necessary in order to secure accurate results, see Fuel by Herman Poole; Mahler, Bulletin de la Societe de L'Encouragement de L'Industrie; Bertholet, Mechanic Chemique and Longuimine, Bestimmung der Verbrennungs Warme.

THE ANALYSIS OF FURNACE AND FUEL GAS.

In metallurgical work two classes of gas mixtures have to be analyzed: first, the gas from chimneys, flues, blast furnaces, etc., representing products of combustion; second, the various gases used as fuel, such as "producer gas," illuminating gas, natural gas, etc.

The gases of the first class are usually tested for the purpose of investigating the nature and the completeness of the combustion in the furnace; those of the second class for the purpose of determining their fuel value and freedom from injurious impurities.

The methods which follow are for the rapid analysis of these gases, and give sufficiently accurate results for furnace control. For fuller information on the general subject of gas analysis, and for the more exact methods with mercury as the containing fluid, the student is referred to W. Hempel's Gas Analysis, translated by Dennis, and to Clemens Winkler's Technical Gas Analysis.

THE ANALYSIS OF FLUE GAS.

Flue gas contains CO_2, O, CO, N, and sometimes small percentages of SO_2 and hydrocarbons. The gas is usually saturated with water vapor, but this is not considered in the analysis, which refers only to the dry gas. The percentage of water in the saturated gas can be calculated from the temperature; if the gas is not saturated, its "dew point" (the temperature at which moisture begins to condense from the gas) must be taken, and the tension of the water vapor it contains found from this. If the temperature of the gas is above the boiling point of water, draw a measured volume of it through a condenser, taking the temperature of the saturated gas as it comes out.

Weigh the water collected from the condenser and add to it the moisture remaining in the gas, as calculated from its temperature after the cooling.

Only the CO_2, CO and O are usually determined in flue gas, the remainder being considered as N.

In making the analysis, a measured volume of the gas is treated successively with a series of reagents that absorb the several constituents, the remaining volume being measured after each absorption. The gas is measured in a graduated tube, which must be

surrounded with a water jacket to keep the temperature constant during the time taken for the analysis.

The gas is always measured at the atmospheric pressure. As the time taken for the analysis is very short, it is assumed that the temperature and the barometer remain constant during the period.

Sampling the Gas.—The gas should be drawn from the flue by a pipe that crosses it at right angles and extends to within six inches of the further wall. The end of the tube should be closed with a cap, and the gas should be drawn into it through a number of holes about $\frac{1}{16}$ of an inch in diameter, drilled along the side of the tube at regular intervals not greater than six inches. The nearest holes should not be less than six inches from the side of the flue. The diameter of the tube should be at least twelve times the diameter of the holes in the side. This will insure a uniform sampling across the flue.

The writer has carefully tested this point by inserting such a tube in air and gas for different portions of its length and analyzing the gas drawn from the tube. The composition of the issuing mixture was always proportional to the number of holes in the gas and in the air, air and gas being under atmospheric pressure.

The sampling tube can be made of iron if the temperature of the flue does not exceed 340° C, as at that temperature iron, even if rusted or covered with soot, is without action on flue gas, neither the CO nor the CO_2 being affected. This point was tested by the writer by passing flue gas containing CO through a glass tube filled with iron tacks, also with rusted tacks and with soot and tacks. The tube was immersed in a bath of melted lead, and the temperature of the lead measured by a nitrogen filled high temperature thermometer. If soot and rust are present on the iron, action begins about 340° C and is rapid at 400° C, CO being oxidized by the Fe_2O_3 and O consumed by the soot forming CO_2. With clean iron, however, there is practically no action at 400° C. As 340° C is above the temperature at which most flue or blast furnace gas is drawn off, the use of iron tubes is generally permissible. For flue temperatures higher than 340° C, water-cooled tubes must be used for withdrawing the samples. For rapidly withdrawing a single sample from the interior of a furnace, an iron tube, open at the end and wrapped with a quarter of an inch of sheet asbestos tied on with wire, can be used. The asbestos cover is well soaked with water and the tube run into the furnace

and the sample drawn. A tube so protected can remain in a white hot furnace for two or three minutes without the asbestos drying or the tube heating beyond a safe point. Where there is a strong draft, as in a chimney flue, it is important that the opening by which the tube passes through the wall be well plastered up with clay, or air may be drawn in and reach the nearer holes and affect the sample. From the end of the sampling tube the gas is drawn continuously by a water or steam aspirator. If the gas sample is to be kept any time before analysis, it must be borne in mind that gases containing CO_2 cannot be preserved over water, as the CO_2 is rapidly absorbed. If the water is saturated with salt, the solubility of CO_2 is somewhat diminished, and what is more important, the rate at which the gas is taken up is much reduced. Hence, brine should be used when the gas has to be kept over a liquid for more than a few minutes. Samples cannot be kept unaltered in rubber bags.
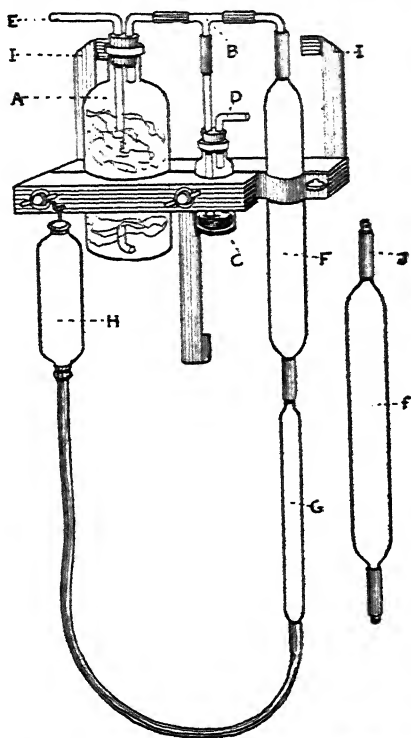
In most cases it is possible and far preferable to make the analysis at the furnace, especially where a series of analyses is required. Where this is not possible, as, for instance, on a locomotive engine test, the apparatus shown in Fig. 11 will be found very effective and convenient for drawing a series of samples at short intervals.

The sample tube, F,f, has a capacity of about 200 c.c.; the ends are closed with rubber tubes stopped with short glass rods J. A number of these sample tubes are provided; they are kept in a rack in a box, and are filled with water before starting out. In the apparatus itself: A is a bottle of about a litre capacity, containing absorbent cotton to filter the gas. C is a small bottle containing a little mercury; it serves as a trap to prevent reversal of the gas current. The gas enters through E, and is drawn out

FIG. 11.—Portable Gas Sampling Apparatus.

through D by an aspirator a the rate of about 150 c.c. at minute.

Thus the bottle, A, will always contain a gas representing the average of several minutes. H is a "pressure bottle," connected as shown.

In taking the sample the apparatus is set up as shown; the gas is supposed to be flowing freely through the bottles A and D. A pinch cock (not shown) on the rubber connection between the Y tube and the sample tube is opened and gas drawn in by lowering the pressure bottle, H, until the gas fills the tube and also the lower tube, G. The cock is then closed and the pressure bottle lifted, so as to put the confined gas under a little pressure; but the lower tube, G, must contain gas enough to prevent any water getting into the sample tube. The rubber connection with F is now pinched tight and the tube disconnected. It is then closed by inserting the glass rod into the rubber. The lower end is closed in the same way. The rubber tubes and stoppers on the sampling tube can be wired if necessary to keep them tight. As the gas is under a little pressure, any leakage during the disconnection will be out and not into the gas.

The tube is now replaced by a second one and the apparatus is ready for drawing a new sample.

Fig. 12 shows a convenient arrangement for drawing a single sample rapidly; as, for example, through an asbestos covered pipe such as was described.

The bottle C contains a little mercury and serves as a trap. The bottles A and B contain brine. The gas delivery tube is connected with the tube F. B is filled with water by raising A, the air escaping through the mercury in C. Now A is lowered and the gas drawn in through F, the mercury preventing any return through E. In this way the gas can be drawn and emptied till all air is expelled, and then the bottle B filled and the pinch cock D closed and the sampler removed.

FIG. 12.—Gas Sampling Apparatus for Single Sample.
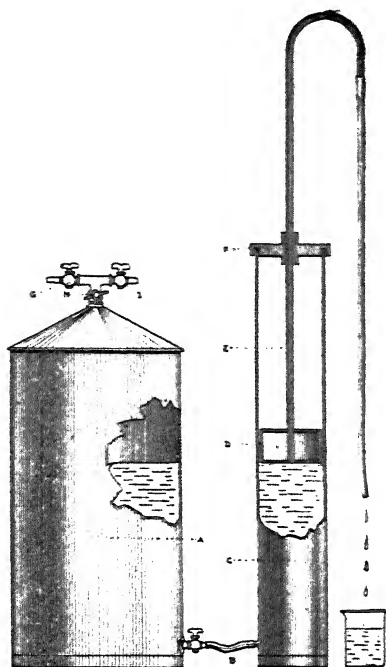
FIG. 13.—Continuous Gas Sampler.

If it is desired to draw a sample continuously for several hours, the apparatus shown in Fig. 13 can be used. It will draw a sample at a nearly fixed rate per minute for several hours. It should be filled with similar gas for some days and then emptied before use, as a new metal gas holder affects the sample a little at first.

The gas is drawn into the tank, A, through the cock, G, by the escape of the water at the bottom through the tube, B. The rate of this escape is kept uniform by the floating siphon, E, in the connecting cylinder, C. The tube, B, is large, so that the level of the water in the tank and the cylinder is the same, and the rate of flow from the latter is regulated by the constant head of the floating siphon carried by the float, D.

In analyzing the flue gas on boiler tests, one sample should be taken every thirty minutes. This will give a fairly accurate average for the period of ten hours usually covered by the test. Experiments made by Mr. F. Haas in the Department of Metallurgy, Ohio State University, showed practically no difference in the results obtained by averaging samples taken every thirty minutes and every fifteen minutes for ten hours. Samples taken in the continuous sampler above described always show less CO_2, but otherwise agree closely with the average of the half-hour samples covering the same ten hours, provided they are analyzed promptly. If the sample in the tank is allowed to stand for some time, the loss of CO_2, with a corresponding increase of N and O, may be very marked. The following two analyses illustrate the comparison for a ten hour test. It shows the loss of CO_2

	Average of 30-minute Samples.	Gas from Tank.
CO_2	11.1	10.4
O	8.0	8.25
CO	0.43	0.30
N	80.47	81.05
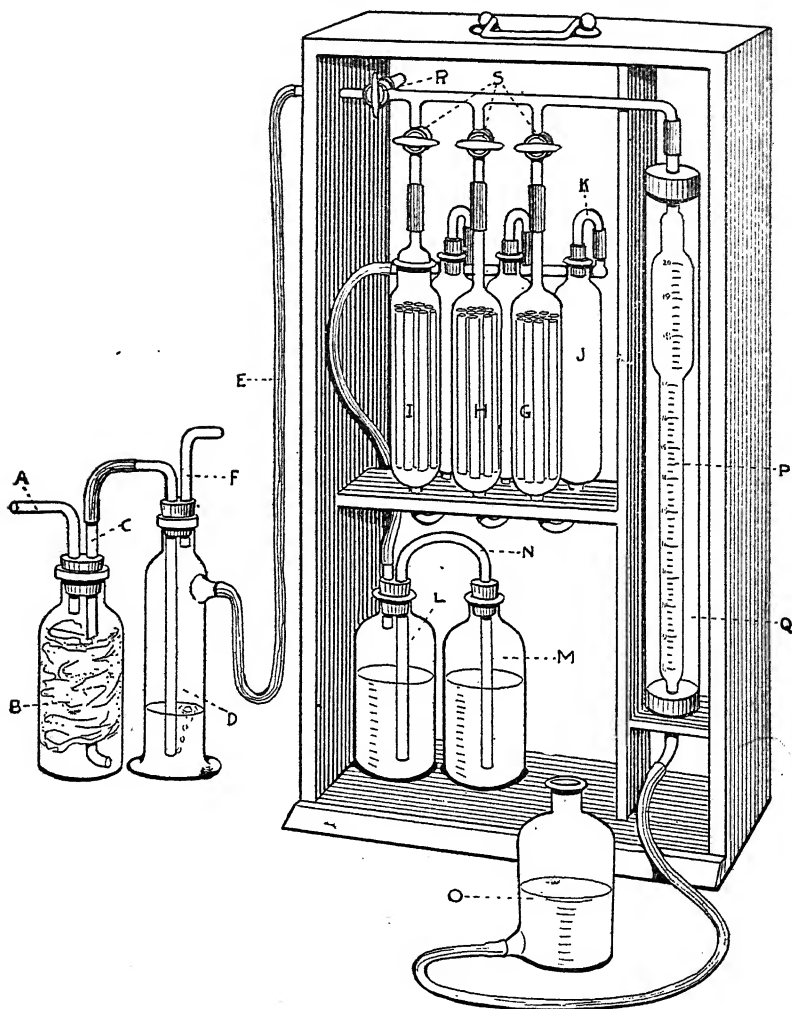
FIG 14.—Orsat's Apparatus for the Analysis of Flue Gas.

Apparatus.—The Orsat's apparatus is the most rapid and convenient for the analysis of flue gas. It is shown as connected for use in Fig. 14. The gas from the flue is drawn into the bottle B through the tube A. B contains absorbent

cotton to filter out soot from the gas. From B the gas passes down into the bottle D, where it bubbles through about an inch of water and then goes through F to the aspirator. If the rate of aspiration is about 150 c.c. a minute, and the bottle B of 500 c.c. capacity, D will contain a sample of the gas representing the average of some minutes. D is connected with the analyzing apparatus as shown. In the apparatus P is the gas measuring tube. Q is the water jacket. S shows the glass stop cocks that connect the gas tube with the reagent tubes, I, H and G. These contain short lengths of glass tube to spread out the liquid and increase the active surface.

L and M are bottles arranged as a water seal to keep the air from the reagents in the tubes ; they are connected with the rear bulbs of the tubes as shown. R is a three way cock that serves to empty the gas from the apparatus. O is the pressure bottle for manipulating the gas in the measuring tube.

The apparatus should be protected from drafts of cold air, but as the analysis is completed in fifteen minutes the water jacket on the measuring tube will prevent any appreciable change in temperature if ordinary care is used. All the stop-cocks should be well greased with vaseline. Two or three drops of H_2SO_4 should be added to the water in the pressure bottle as this prevents it from becoming slightly alkaline and absorbing CO_2.

The water in the pressure bottle must be saturated with the gas to be analyzed, so as to prevent its acting on the sample. This is best done by running several analyses before the regular work begins. This will bring the water to a condition of saturation with the average gas and render it practically non-absorbing to the gas analyzed. Once in this condition the water can be used indefinitely. If new water is put in the saturation must be repeated.

Preparation of the Reagents.—KOH Solution. Dissolve 100 grams of the best quality potassium hydroxide in 300 grams of water. Let the solution stand in a closed bottle till any oxide of iron settles, and use only the clear solution. It is best to prepare a quantity of this and keep it some time before use.

Pyrogallic Acid. Use only the white resublimed acid.

Cuprous Chloride Solution. Dissolve 12 grams of pulverized and recently ignited CuO in 125 c.c. of concentrated HCl. Next dissolve 40 grams of crystallized $CuSO_4$, $5H_2O$ in about 200 c.c. of water, adding a few drops of H_2SO_4. Cool this solution and add 12 grams of granular zinc (such as is used in the reductor; see page 36). Add this carefully to avoid too violent effervescence. The copper precipitates as a brown powder. When all the zinc is dissolved, let the copper settle, decant off the liquid closely and wash by decantation till free from zinc sulphate. If the zinc does not dissolve readily, add a little more H_2SO_4. Pour off the liquid as completely as possible from the precipitated copper and add the solution of CuO in HCl. Stir it up thoroughly for some minutes, pour off the solution from any undissolved copper, and keep it in a bottle containing strips of metallic copper. The bottle must be well corked, and a little concentrated HCl should be added from time to time.

To fill the apparatus: Remove the old solution by first driving air over from the gas tube into the absorbing bulbs. This is done by raising the pressure bottle and forcing the liquid all into the rear bulbs. Then empty each by a small siphon first filled with water and inserted down to the bottom of the bulb. Now fill the first rear bulb, J, with the KOH solution. This serves to absorb CO_2 and also SO_2 and H_2S. It acts rapidly and completely and one filling will serve for from fifty to sixty gas analyses before its action begins to be too slow.

Put a good sized funnel into the second rear bulb and weigh into it 15 grams of pyrogallic acid. Wash this down into the bulb with 150 c.c. of KOH solution of the same strength as was used in the first tube. If the apparatus will not hold this volume of solution, take less and reduce the pyro proportionately.

The alkaline pyro absorbs oxygen, forming an intensely colored

liquid. It acts rapidly at first, but as it becomes saturated it works more slowly. One filling usually serves for about thirty analyses before its action becomes too slow.

The relation of the pyro to the alkali is important. If too little KOH is used, the solution is liable to give off CO on absorbing O. With a solution prepared as directed, no CO will be given off when the percentage of O is no larger than is found in flue gas or air; but if a gas is to be analyzed that contains high percentages (40 or 50 per cent.) of O, it will give off CO. In this case it is necessary to use a much stronger KOH solution and less pyro. See Clowes. Jour. Soc. Chem. Ind. 1895. p. 1065.

The third bulb is filled with the cuprous chloride solution. When fully reduced, the CuCl solution is nearly colorless, but is usually dark brown from the presence of a little $CuCl_2$. The glass tubes in this bulb contain spirals of copper wire, which keep the solution reduced.

The copper is slowly dissolved by the $CuCl_2$ formed. The solution is liable to become oversaturated, so that a granular precipitate of CuCl will separate. This will sometimes clog the tube so as to interfere with its action. It must be carefully cleaned out and the apparatus refilled. It is important that this solution be carefully kept from air, as it absorbs oxygen very rapidly, forming $CuCl_2$ and using up the excess of HCl. If this solution is diluted with water, it deposits a heavy precipitate of CuCl, which is very sparingly soluble.

The strong HCl in this solution gives off vapors which increase the volume of the gas. In accurate work these should be removed by running the gas over into the KOH solution and back before measuring its volume. The CuCl absorbs CO rather rapidly. Its capacity is not very large, but as the amount of CO in flue gas is small, one filling will serve for a large number of analyses. It should be changed as soon as its action becomes slow. As it absorbs oxygen as well as CO, it must never be used until the oxygen has first been removed from the gas.

Making the Analysis.—Fill all the reagent bulbs to the mark on the capillary tubes by opening the proper stopcocks and lowering the pressure bottle carefully till the liquid rises to the right point. Do this with one bulb at a time, and on no account try to set the level of the liquid by opening or closing the stopcocks. Bring it to the right

point by raising or lowering the pressure bottle, and then close the stopcock. Proceeding in this way, the fluid will never be drawn up into the stopcock. Should such an accident happen, the stopcock must be immediately taken out, washed, and then relubricated with vaseline. The alkaline liquid, if allowed to remain in the glass stopcock, would soon cause it to stick hopelessly. Now set the three way cock so that the opening to the side is connected with the measuring tube. Raise the pressure bottle till the liquid fills the tube to the mark on the capillary. Turn the cock so as to close this connection and open the one to the sample inlet tube, lower the bottle and draw in slowly 50 or 60 c.c. of gas. This should be enough to completely wash out air in the connecting tubes. Again reverse the stopcock, lift the bottle and run this gas, which is contaminated with that left in the connections and capillaries, out through the side tube. Now again reverse the stopcock and draw in the sample of gas for analysis, lowering the bottle until the gas fills the measuring tube to some distance below the zero mark. Close the cock and set the pressure bottle on a support a little above the level of the zero point. Pinch the rubber tube near the bottom of the burette, open the cock to the side and carefully let the liquid run in by releasing the pressure of the fingers until it reads exactly zero on the tube. Now close the cock carefully, take down the bottle, and read the volume of the gas after equalizing the pressure by bringing the surface of the liquid in the bottle to the level of that in the tube. The reading should be exactly zero. If it is 0.1 or 0.2 c.c. off, this can be corrected by raising or lowering the level of the water in the pressure bottle until the reading is zero, and making all subsequent readings in the analysis after giving the leveling bottle the same relative elevation.

The measuring tube now contains 100 c.c. of gas. Open the stopcock into the potash bulbs and run the gas over by raising the pressure bottle. Be careful to so hold the bottle

that the liquid will rise only to the mark in the gas tube Now draw the gas back in the same way, run it over again and again back. Bring the potash solution carefully to the mark in its tube, close the stopcock, wait at least thirty seconds for the liquid to drain down the side, level as before and read the volume. Transfer a second time to the potash, draw it back and read the volume again. If it does not agree with the first reading, run it over a third time. With fresh potash solution, the second reading should always check the first. The decrease in volume is the CO_2. Now proceed in the same way with the other tubes, using the pyrogallic acid first and then the cuprous chloride. With the pyro tube, the gas should be run over two or three times rapidly before taking a reading, so that the dark saturated solution forming on the walls of the bulb may not remain long in contact with the gas; as this might lead to the formation of CO. The liquid draining down the side of the bulb will show by its change of color when it is absorbing oxygen. As soon as the oxygen is all absorbed, the liquid on the sides of the bulb will not turn brown as the gas reaches it. Always get two readings that agree before proceeding to the next tube. The corresponding decreases in volume give the oxygen and the CO. The residual gas is estimated as N. It will contain any H and CH_4 present in the original gas, but these are rarely present in chimney gases in measurable amounts. When the analysis is finished, run out the residual nitrogen, leaving the measuring tube full of water. Now everything is ready for the next test.

Extreme care should be taken to avoid getting any of the absorption solutions into the connection or measuring tubes. Should this happen, they must be washed out and the water in the pressure bottle changed before starting a new analysis, as gas might be absorbed in filling the apparatus. The Orsat's apparatus may be used for the determination of CO_2 and CO in the gas from the iron blast furnace. In this case the residual gas invariably contains hydrogen and methane and should be kept for further analysis.

THE ANALYSIS OF FUEL GAS AND ILLUMINATING GAS.

These gases contain CO, H, CH_4 (methane), unsaturated hydrocarbons principally C_2H_4 (grouped together as the "illuminants,)" N, O, CO_2, and traces of H_2S. The illuminants are the constituents that give the illuminating power to the gas. The gas usually contains in addition a certain amount of benzine and other hydrocarbon vapors and traces of CS_2. In producer gas the principal components are N, CO and H; in water gas, CO and H; in illuminating gas, H and CH_4; while natural gas consists almost entirely of CH_4. The gas sample is usually brought to the laboratory in tubes or bottles such as have been already described. As the percentage of CO_2 is small, the gas can be kept for a short time over water, unless hydrocarbon vapors are present. These would be rapidly washed out in contact with water. Gas containing them must be collected in dry tubes and kept warm till analyzed, or better taken directly into the apparatus from the gas main.

As the analysis of these complex mixtures requires considerably more time than the work in the Orsat's, it is not safe to regard the temperature as constant during the analysis. A thermometer must be placed in the water jacket surrounding the measuring tube and read every time the gas is measured.

The variations in temperature during the course of the analysis can then be allowed for by correcting the corresponding readings so as to bring them to what they would have been had the temperature remained the same as that at which the original volume was measured. This can be done by the following formula:

$$V = V' - V'\frac{(t' - t)}{273 + t'}$$

in which V is the volume at the temperature t, and V′ the volume at the temperature t′. Variations in the barometer need not be considered, as they are rarely important during the time taken for the analysis.

DESCRIPTION OF THE ELLIOTT APPARATUS AND THE PROCESS OF ANALYSIS.

The Elliott apparatus, as shown in Fig. 15, is used in the processes which follow. It is convenient and sufficiently accurate for most technical work. It consists of a gas burette, A, surrounded by a large glass tube, B, filled with water in which a thermometer, C, is immersed. The burette is
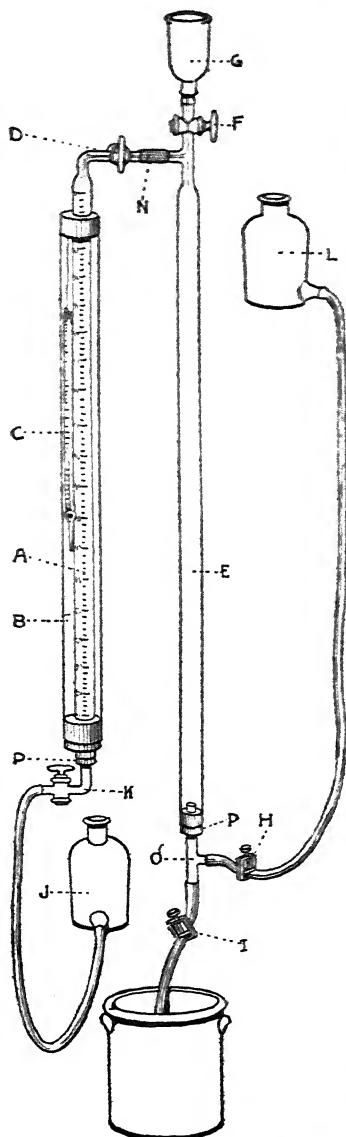
FIG. 15.—Elliott Apparatus for the Analysis of Gases.

graduated to tenths of a cubic centimeter and holds 100 c.c. from the zero mark to a point marked on the capillary tube at the top. This capillary is provided with a stopcock, D, and connects at N with the absorption tube, E. The joint at N must be easily detachable. It is made by slipping a piece of thick soft rubber tubing over the two capillary tubes which meet at this point. The absorption tube, E, is not graduated and is slightly larger than A. The two-way capillary tube at the top serves to connect it with A and also through the glass stopcock, F, with the air. The top of this tube is conical and ground into the detachable cup, G, which holds the reagents which are to be applied to the gas. The cup can be lifted off and a rubber tube slipped over the end of the capillary for drawing in the gas sample. The bottom of the gas burette, A, is connected with a pressure bottle, J, by means of a rubber tube and the glass stopcock, K, the tube of which passes through a rubber stopper in the bottom of A. This stopper should be carefully wired to the tube so as

not to slip out.   The bottom of E is connected with a similar pressure bottle, L, and also a drain tube, I, for emptying the tube.   These tubes are closed by the pinchcocks, H and I.

See Chemical News, vol. XLVIII. p. 189, and School of Mines Quarterly, Nov., 1881.

In making gas analyses with apparatus in which water is the containing fluid, the error from absorption of the gas by the water will be greatly diminished if care is taken to have the water used saturated with the gas to be treated, as was mentioned in connection with the Orsat's.   On this account the water in the pressure bottle, J, and that used in the gas pipettes and receivers described later should not be changed except when necessary, and when changed the new filling should be saturated by running similar gas over and back a number of times before beginning the analysis.

Manipulating the Apparatus.—The measuring tube should be thoroughly clean and the apparatus set up as shown.   It is convenient to have it permanently placed in a situation where the temperature is reasonably constant.   The bottles L and J are filled with distilled water to which a drop of H_2SO_4 is added.   Fill the burette, A, by opening K, D and F and raising the bottle J; then close D and fill E clear to the cup, G, by opening H and raising L; then close the stopcock F.   Now fill the drain tube with water by opening I and letting water run through from the pressure bottle, F, until all air bubbles are driven out.   If any air is left in the drain tube it may work up into the gas.

Taking the Gas Sample.—Remove the cup, G, attach the rubber tube, bringing the gas to the end of the capillary tube above F.   Be careful to run some gas through the rubber tube first to drive all air out.   Now, the bottle L being lowered, open F until 30 or 40 c.c. of gas have run into E. This serves to wash the air out of the connections.   Close H and open D and F, lowering J until the burette is filled to below the zero point.   Now close D and F and remove the gas tube.   Now raise the bottle J until the liquid reads zero in the burette (due to the extra pressure) and close K. Now raise L above the liquid in E.   Open H momentarily

(to cause a surplus of pressure in D and prevent suction of air). After closing H, open first F and then D, allowing the excess of gas to escape, and immediately close them again. This leaves 100 c.c. of gas in A under atmospheric pressure. Test the reading by opening K and leveling the water in the bottle and the burette. It should read zero. If below zero, repeat the process; if above zero, the analysis can be made on the volume present or a new sample can be drawn in order to avoid calculations.

Now replace the cup and fill the tube, E, to the end of the capillary by raising L; then close F. Run the gas over into the absorption tube, E, by opening D, K, and H, raising J and lowering L. Do not let the capillary tubes fill with the liquid; merely bring it up into them. Now close D.

The absorbing reagents are applied to the gas by pouring them into the cup, G, carefully opening F and letting the liquid run down the capillary and then down the sides of the tube E in a thin sheet. The absorbents are used in the following order: First, *Absolute Alcohol*. This absorbs hydrocarbon vapors. Only a small quantity must be used, as it absorbs the permanent gases to a certain extent. The alcohol vapor must be washed out of the gas after the application of the reagent, or its tension will cause error. Second, *Potassium Hydrate* for CO_2, H_2S, and SO_2. Third, *Bromine Water* for "illuminants." The bromine vapors left in the gas must be absorbed by KOH before measuring the gas. Fourth, *Alkaline Pyrogallate* for oxygen. The solution is the same as that used in the Orsats. It should be prepared shortly before use and kept in a well stoppered bottle. Fifth, *Cuprous Chloride* for CO. This is prepared and kept as previously directed.

The required amount of the reagent is poured into the cup, the bottle, L, being set a little lower than the level of the liquid in the tube, so that the gas may be under slightly less than atmospheric pressure. This will prevent any

escape of the gas through the capillary when the stopcock is opened to admit the reagent. See that the pinchcock, H, is open and I closed. Now cautiously open F, allowing the reagent to run in slowly and spread out in a thin sheet on the walls of the tube. When the reagent has nearly all run in, but before any air enters the capillary, close the stopcock, F. Now pour a little water into the cup and run it in in the same way, closing the pinchcock, G, and opening I carefully to let the excess of liquid escape. This washing may be repeated if necessary. Now, I and F being closed and H open, raise L, open D, and run the gas back into A for measurement. Close B, being careful that none of the liquid in E runs into the capillary, but stops just below the cross tube. The tube E is now full of liquid mixed with an excess of the reagent. Empty it as follows: Close H and open I and F and let everything run out through the drain tube into a slop jar. Wash the tube by pouring water into C and letting it run out through I. Now close I and refill the bottle, L, open H and fill the tube, E, as in the beginning. After re-transferring the gas to E the apparatus is ready for the next reagent.

Do not read the volume of the gas in the burette for at least two minutes after transferring. In reading, carefully level the liquid in the tube and in the pressure bottle. Let the tube drain two minutes longer after the first reading and read again. If the readings do not agree, read a third time. Immediately after taking the reading of the gas volume, read and record the thermometer in the water jacket.

Special Notes on Each Determination.

First, Hydrocarbons. Use 3 c.c. only of alcohol, As it is important that the alcohol be free from water, the cup and the end of the capillary must be wiped dry before putting it in.

After putting the reagent into the cup do not allow time for the water in the capillary above F to diffuse into it but immediately open the cock and let enough run into the tube to drive the water before it. This first addition of alchol will drive the water down the sides of the tube E and leave them almost perfectly dry so that when

the rest is allowed to run in it will act without any appreciable dilution with water. After the alcohol has been run in, carry out the rest of the process rapidly so that the liquid hydrocarbons which tend to separate when the alcohol mixes with the water at the bottom may not have time to go back into the gas. After adding the alcohol wash once with 5 c.c. of water, run over into the burette, empty and clean the tube, E. Now refill the tube, E, with fresh water, run the gas back, and wash it again with 5 c.c of water. This takes out the alcohol vapor with a minimum amount of wash water.—a point of importance if the gas contains CO_2. *Second, CO_2.* Use 3 to 4 c.c. of KOH solution. Wash with 5 to 10 c.c. of water and transfer. Retransference is not necessary, as one washing is sufficient. *Third, Illuminants.* Use 3 to 4 c.c. of saturated bromine water, letting it act for several minutes; then wash down with 5 c.c. of water, and then with 2 to 3 c.c. of KOH solution to remove the bromine fumes. Then wash with 5 c.c. more of water, transfer and measure. *Fourth, Oxygen.* Use 5 c.c. of pyro solution. Let it run in very slowly. Wash with 5 c.c. of water, transfer and measure. If more than 3 per cent. of oxygen is present, repeat the treatment with pyro, as one treatment may not remove it entirely. *Fifth, Carbon Monoxide.* Use 5 c.c. of CuCl solution and wash with 5 c.c. dilute HCl and then with 5 c.c. of water. After washing, run in 2 c.c. of KOH solution to absorb HCl vapors, and wash again. Transfer and read the volume. Now, after cleaning out the absorption tube, test the gas again with the CuCl. If it shows a further absorption of more than 0.2 of a c.c., give it a third treatment. The determination of CO is not very satisfactory unless the gas is treated repeatedly with the reagent. After the CO determination there will be a considerable precipitate of CuCl in the absorption tube. This must be washed out first with dilute HCl and then with water.

THE DETERMINATION OF HYDROGEN AND METHANE BY COMBUSTION.

The gas remaining unabsorbed consists of methane, hydrogen, and nitrogen. Its analysis depends on the following properties: First, when a mixture of hydrogen and methane with a considerable excess of air is passed over finely divided palladium at a temperature of 80° to 100° C, the hydrogen is completely oxidized to H_2O. The methane is not affected unless the temperature is very considerably higher. If any CO should be present in the mixture, it is oxidized to CO_2. As two volumes of hydrogen unite with one volume of oxygen to form water which condenses, the hydrogen in the gas is equal to two-thirds of the contraction in volume following this combustion. Second, when a mixture of methane and hydrogen is

burned at a high temperature with an excess of oxygen, the product is CO_2 and water. The volume relations are as follows: One volume of CH_4 plus two volumes O produces one volume CO_2 and two volumes H_2O vapor which condenses. One volume H plus 0.5 O produces one volume H_2O vapor which condenses. Hence, if pure CH_4 is burned with oxygen, one-half the contraction is CH_4; and if the CO_2 produced is absorbed by KOH, the further contraction will equal the CH_4, or one-third of the total contraction is CH_4.

When a mixture containing a known amount of H and an unknown amount of CH_4 and N is burned, the amount of methane is found by subtracting ⅔ of the hydrogen from the contraction and dividing the remainder by 2. If the CO_2 is absorbed and then the total contraction measured, the CH_4 is equal to this minus ⅔ of the hydrogen and divided by 3.

Process for Hydrogen.—*Preparation of the Palladium Asbestos Tube.*—See Winkler's Technical Gas Analysis, p.77. A weighed amount (0.2 to 0.5 gram) of metallic palladium is dissolved in aqua regia, an excess of HCl added, and the solution evaporated to dryness on a water bath. The $PdCl_2$ is then dissolved in a very little water, an excess of a cold saturated solution of sodium formate added, and enough Na_2CO_3 to make the liquid strongly alkaline. Now absorb the liquid in very soft, long-fibered asbestos, using the same weight of asbestos as of the metal taken. Dry the whole at a gentle heat, and when thoroughly dry wash the black mass very carefully with warm water till all the soluble salts are removed. Again dry
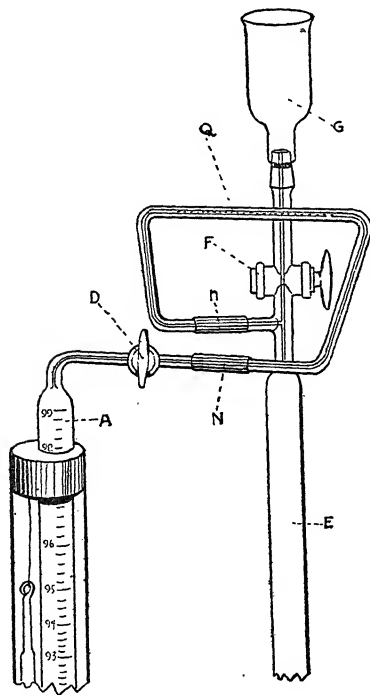
FIG. 16.—Palladium Tube as connected for the Determination of Hydrogen.

thoroughly. The soft black material contains 50 per cent. of finely divided palladium, and when dry will cause H and O to combine at ordinary temperatures. To prepare the combustion tube, take a straight piece of capillary tubing of about 1 mm. bore and 5 mm. thickness. Draw out some of the prepared asbestos into a narrow strand, moisten it and carefully roll it with the fingers into a small thread about two inches long, which will go into the tube. Hold the latter vertically and carefully slide the little thread into it. Now by putting a drop of water into the tube the thread of asbestos can be shaken down to the middle; the water must now be carefully dried out by gentle heating. Do not boil it or it will tear the asbestos to pieces. The ends of the tube are then heated and bent so that it can be connected between the gas burette and absorption tube, as shown in Fig. 16. In the cut, Q is the thread of palladium asbestos; N and n, the connections with the gas burette, A, and the absorption tube, E.

The Determination of the Hydrogen in the Residual Gas.
As the gas has to be mixed with a large volume of air in order to burn the H, not more than 25 c.c. can be used; the remainder must be removed from the burette. It can be kept for the determination of the methane.

The extra gas is taken out into a gas holder or pipette like the sampling tube shown in Fig. 11, only smaller. It has a pressure bottle attached at the bottom and a stopcock in the capillary tube at the top. This tube should be bent at right angles. In place of the stopcock a rubber tube and pinch cock can be used.

To draw off the gas, fill the pipette to the top of the tube with water by lifting the pressure bottle, and then close the cock. Detach the absorption tube in the Elliott apparatus at the joint in the capillary, N (Fig. 15), from the burette containing the residual gas, the cock D, being closed. Now attach the gas pipette by a rubber connection in the same

way that the tube E was joined, taking care to include no air, but filling the rubber connection with water before inserting the tubes. By opening the cock, D, and lowering the pressure bottle of the pipette the gas can be drawn over.

Draw off in this way a little less than three-fourths of the residual gas. Now close the cock, D, and the cock of the gas pipette and disconnect the two. Keep the gas in the pipette for the determination of the methane.

Now bring the volume of the gas in the burette to exactly one-fourth of that of the original residue by the same method as was used in taking the original sample. This takes little time and saves trouble in the subsequent calculations. Now lower the pressure bottle, L (Fig. 15), and draw enough air into the burette to insure an excess after burning all the hydrogen. Three times the volume of the gas is usually sufficient.

Read the volume of the air plus gas in the burette, and then connect up the apparatus with the palladium tube, as shown in Fig. 16. Warm gently the portion of the tube containing the palladium to a temperature not exceeding 100° C, with a small alcohol lamp, and slowly run the mixture of gas and air over the palladium into the absorption tube, and then back again into the burette, keeping the palladium asbestos warm all of the time. The rate of flow must not exceed 15 to 20 c.c. per minute. After the combustion allow several minutes for the gas to cool, and then measure the volume. Now run it over the heated asbestos again, and again read the volume. If the two readings differ by more than 0.5 c.c., run it over again.

The difference between the volume of the gas plus air and the volume after combustion is the contraction due to the combustion of hydrogen. Two-thirds of this contraction equals the volume of the hydrogen, and as one-fourth of the residual gas was taken for the test, four times this value will give the H in the original gas.

After the combustion, remove the palladium tube, connect up the burette and the absorption tube in the ordinary manner. and test the gas for CO_2. If any is found, it indicates either that some CH_4 was burned, in which case the palladium tube was heated far too hot, or that there was CO in the residual gas which had escaped absorption by the cuprous chloride and was burned by the palladium. If more than 0.4 c.c. of CO_2 is found, the determination should be duplicated on a second portion of the residual gas in the pipette, taking more care in heating the palladium. If the CO_2 is still found, it may be assumed that it is due to the presence of CO. The error in the hydrogen will be one-third of the volume of the CO present in the gas. and hence may be neglected if the amount of the CO_2 is less than that stated.

There is practically no danger of explosion when H is burned with air by palladium in the manner described. If oxygen gas is used the danger is considerable. and in this case the apparatus must be surrounded by wire gauze and glass as described for the methane burner. It is well always to protect the eyes in some way when making the gas analyses by combustion, even when air only is used.

The Determination of the Methane.—There is needed for this determination : first, oxygen free from all impurities except nitrogen; second, an electric current of sufficient power to heat a spiral of fine platinum wire to a bright red heat, and so controlled by a rheostat that it can be increased or diminished as needed; third, the special " Methane Burner " shown as connected up for use in Fig. 17.   S is a glass bulb of about 150 c.c. capacity connected with the pressure bottle, L, by means of the side tube, U, and having at the top a capillary tube and stopcock, R, for connecting it with the measuring tube of the Elliott.   T is a spiral of fine platinum wire, which can be heated by the current brought in through the wires, W, passing through the rubber stopper, V.

As there is always some risk of explosion, the burner must be surrounded by a cylinder of wire gauze and one of glass, as is shown in the cut, to protect the operator.

During the combustion the current must be reduced, or the added heat of the burning gas will make the wire so hot
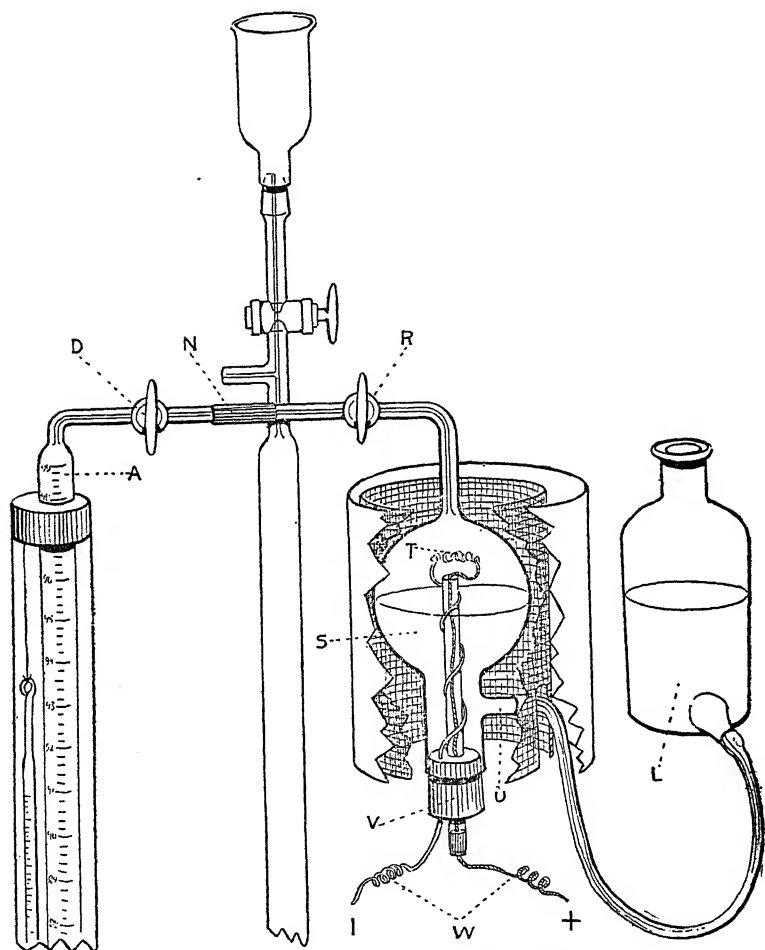
FIG. 17.—Apparatus for the Determination of Methane.

that it may fuse or crack the glass. The glass is also liable to be cracked if the wire is placed too near it.

Process.—Transfer to the measuring tube of the Elliott apparatus another quarter of the residual gas in the pipette and measure it accurately. Now fill the methane burner with water to the end of the capillary, attach it to the

Elliott burette, run the measured gas into it, close the stop-cock, R, and detach it from the burette. Now draw into the measuring tube of the Elliott, 60 to 70 c.c. of oxygen. Let it stand until it attains the temperature of the water jacket and read the volume very carefully. Now connect the burner containing the gas with the burette containing the oxygen, in the manner shown in the figure. Heat the platinum spiral to a yellow red heat by turning on the electric current. Now gradually run the oxygen from the measuring tube into the methane in S; the rate must not exceed 15 to 20 c.c. per minute. Keep the spiral at a steady red heat by regulating the electric current. The gas will burn quietly and without any explosion if the operation is carefully conducted. When the gas has all been run in, cut off the current, allow the apparatus to cool, and run the gas back into the measuring tube of the Elliott. Let it stand till it attains the temperature of the water jacket and read the volume carefully. The difference between this volume and the sum of the oxygen and gas taken is the contraction due to the combustion of the methane, hydrogen, and any carbon monoxide present. From this the volume of the methane can be calculated as already indicated. The Elliott is then connected up as usual and the gas treated with KOH for the absorption of the CO_2. This gives a further contraction, which should equal the methane, but, owing to the absorption of CO_2 by the water, is usually too low. The correct percentage is finally obtained by adding the first contraction to the second, deducting the contraction due to the hydrogen present and then dividing the remainder by 3. This gives the volume of methane in the gas treated; and as this represents one-quarter of the original sample, the result must be multiplied by 4 to give the methane in the volume of gas taken for analysis.

The temperature must be carefully read every time the volume of the gas is measured and corrections made, as already explained. Do not fail to give time for the temperature of the gas and the water

jacket to become equal, as well as for the measuring tube to drain. Allow two or three minutes at least for this purpose.

The above processes are sufficiently accurate for most technical work. Where special accuracy is required, the analysis must be made over mercury instead of over water.

The nitrogen in the gas is estimated by difference, subtracting the sum of the volumes of the gases determined from that originally taken. For other forms of apparatus, as well as for the manner of working with mercury, see Smith and Powers, Jour. Soc. Chem. Ind., 1897, p. 400; Dennis and Hopkins, Jour. Am. Chem. Soc., 1899, p. 398.

THE ANALYSIS OF BLAST FURNACE SLAGS.

The slags made in the iron blast furnace are essentially silicates of lime, magnesia and alumina. They usually contain, however, small percentages of iron, manganese, and sulphur. Phosphorus is rarely present in more than traces. Titanium and other rarer elements, if present in the ore, will be found in the slag. Slags that are high in alumina and magnesia, will sometimes contain small crystals of spinel, $(MgOAl_2O_3)$. As this substance is neither attacked by HCl, decomposed by fusion with Na_2CO_3, nor dissolved by HFl, it will be found in the silica obtained in the analysis. Spinel can be decomposed by prolonged treatment with hot H_2SO_4 diluted with its own volume of water.

Most furnace slags can be decomposed by treatment with HCl, especially if they have been suddenly cooled from the molten state. Slags that are not decomposed by HCl must be fused with Na_2CO_3.

Slags frequently contain metallic iron in small grains, this should be taken out of the crushed sample by a magnet. If the slag itself is magnetic the metal grains can be picked out under a magnifying glass with pincers. The sample must finally be ground in an agate mortar to an impalpable powder.

For the purpose of furnace control it is usually sufficient to know the percentages of silica, alumina, lime and magnesia in a slag. These can be determined with sufficient accuracy by the following process.

The Determination of the CaO and the MgO.—Weigh one gram of the sample into a casserole, add 30 c. c. of water and stir the slag up into it to prevent caking and the separation of gelatinous silica on the addition of acid. Now add 20 c. c. of HCl and heat. Everything should dissolve except a few flakes of SiO_2 and possibly a little C or S. There should be no gritty residue. Cover the casserole, and boil the solution to dryness to separate most of the silica.

Now add 10 c. c. of HCl, a few drops of HNO_3, and then 50 c. c. of water. Boil to dissolve the bases and then transfer the contents of the casserole, without filtering, to a 500 c.c. graduated flask. Dilute the liquid to about 300 c.c.

and add NH_4OH until the alumina separates, but avoid a large excess. If the sample contains more than a few tenths percent. of manganese add 2 or 3 c.c. of ammonium sulphide to precepitate it with the alumina. Heat the contents of the flask to boiling and boil for 3 minutes. Cool the liquid and dilute it to the mark with water free from CO_2. Mix the contents of the flask thoroughly and then filter off 250 c.c. through a dry filter.

Determine the lime and magnesia in this volumetrically as in a limestone. If ammonium sulphide was used, add HCl to the filtered solution, till it is neutral and then about 5 c.c. in excess. Boil till the H_2S is expelled then add 0.5 gram of $KClO_3$ and heat till the separated sulphur is dissolved. Now add NH_4OH in excess and proceed with the determination of the lime as before. Should a trace of MnO_2 separate on adding the ammonium hydroxide, continue the heating till it dissolves and the solution is nearly colorless, before precipitating the lime.

The Determination of the SiO_2 and the Al_2O_3.—Weigh 0.5 gram of the sample into a casserole, treat it with water and HCl and evaporate to dryness as before, in this case however the dry residue must be heated till all HCl is expelled, avoiding a temperature of over 120°.

Take up the residue in water and HCl filter off and weigh the silica. It is well to evaporate the solution to dryness a second time before filtering off the silica, as this makes the filtration more rapid.

The residue is usually taken as silica but it is liable to contain traces of Fe_2O_3, TiO_2, and spinel. It may be tested with HFl and any fixed residue deducted, (See p. 70). If this is done the silica should be separated by a double evaporation as it is not all precipitated by a single one. Ordinarily the impurities present will about balance the silica lost and so the gross weight is nearly correct.

The Alumina is now determined in the filtrate from the silica.

In the absence of much manganese this can be done by precipitation with NH_4OH as in the analysis of a limestone, taking care to have plenty of NH_4Cl present and to redissolve the first precipitate which is likely to contain a little lime. The precipitate should be washed by decantation until free from chlorides and then transferred to the filter. The precipitate contains any iron, phosphoric acid and titanic acid in the slag, but as these are rarely present in noticeable quantities they may be neglected.

If the slag contains much manganese the alumina must be separated from it by a basic acetate precipitation as described on p. 73. The precipitate is then redissolved in HCl and the alumina, now free from manganese, precipitated with NH_4OH.

Determination of the Alumina as Phosphate. This method gives good results on iron ores as well as slags and is quite rapid. It is similar to that used in determining the aluminum in steel.

Dilute the filtrate from the silica in a 300 c.c. beaker to about 200 c.c. To the cold solution add about 15 c.c. of a saturated solution of sodium phosphate and then NH_4OH cautiously and with constant stirring until a slight permanent precipitate forms. Now add 5 drops of HCl which should dissolve the precipitate and leave a clear solution. Now add with constant stirring 20 c.c. of a saturated solution of sodium thiosulphate. If much iron is present as in the case of an ore, the solution will turn nearly black but on continuing the stirring will grow lighter as the iron is reduced and finally a white precipitate of $AlPO_4$ will be thrown down mixed with a large quantity of S. Cover the beaker and heat the solution till it boils. When *boiling* add 20 c.c. of a solution consisting of 100 grams of sodium acetate, 200 c.c. of acetic acid, sp. gr. 1.04, and water to make 500 c.c. Boil the solution 10 minutes longer or till the precipitate coagulates.

Let settle and filter, washing the precipitate 10 times with hot water. Put the wet filter into a crucible, ignite at

a low heat to burn off the paper and sulphur and then ignite over the blast lamp.

The residue is $AlPO_4$ and contains 0.418 Al_2O_3.

J. M. Camp, Iron Age 65, 17.

When this method is applied to ores the first precipitate is likely to contain a little iron. This can be removed by dissolving and reprecipitating it in the same way.

Sulphur and *iron* can be determined in slags as in iron ores.

The sulphur in slags is present almost wholly as calcium sulphide. It can be determined approximately by adding 150 c.c. of water to 0.5 gram of the very finely pulverized slag and titrating with the standard iodine solution used for sulphur in iron.

Stir the mixture of slag and water and, add 3 or 4 c.c. of starch solution, then run in the iodine till the blue color develops. Now add 15 c.c. of concentrated HCl, stir and add the iodine again until the color no longer disappears.

If 1 c.c. of the iodine equals .0005 S, each c.c. taken will be equivalent to 0.1% sulphur in the slag.

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It is probably more accurate to evolve the H_2S in a flask as for pig iron. Put 5 grams of granular zinc into the flask, then add 0.25 to 0.5 gram of the very finely ground slag. The hydrogen from the Zn carries over the H_2S from the slag. This is absorbed by an ammoniacal cadmium solution and titrated as usual. See Camp. "Methods of Analysis in the Laboratories around Pittsburg", 2nd Ed. p. 147.

Manganese in slag can be determined as in iron ores. Small percentages are best estimated by the color method.

THE ANALYSIS OF FIRE CLAYS.

Determination of SiO_2, Al_2O_3, Fe_2O_3, CaO and MgO.—
Mix 1 gram of the clay with 8 grams of dry Na_2CO_3. The
purity of this reagent should be tested by running a blank
upon it. Put the mixture in a platinum crucible, and heat
over a Bunsen burner until the mass is sintered together
and caked. Now heat with a blast lamp until the mass fuses.
Keep some minutes in quiet fusion. Cool suddenly by dipping
the bottom of the crucible into water (this will usually cause
the cake of material to come loose so that it can be easily
detached from the crucible). Now put the cake, with the
crucible, into a dish or casserole with water enough to cover
the whole, and wash the cover of the crucible free from all
attached particles. When the mass is disintegrated, remove
the crucible, cleaning it if necessary with a little HCl, which
is then to be added to the body of the liquid. Now add an
excess of HCl to the contents of the dish, which must be
kept carefully covered to avoid loss by "spurting." Warm
until everything is dissolved and effervescence has ceased.
Wash off the cover and evaporate the liquid to dryness on a
water bath, stirring occasionally to break up the gelatinous
silica. When all odor of HCl is gone, add a little water and
again evaporate to dryness. Now add 30 c.c. of dilute HCl
(1 : 1) digest at a gentle heat, and then dilute to 150 or 200 c.c.
Filter off, wash thoroughly, ignite and weigh the SiO_2,
repeat the ignition until the weight is constant. The purity
of the silica must be tested by volatilizing with HFl.

The filtrate should be diluted to 300 c.c., warmed and pre-
cipitated by a slight excess of NH_4OH. Heat to boiling for
not to exceed five minutes and let stand until the precipitate
has settled leaving a perfectly clear liquid. Prolonged boiling
makes the precipitate slimy and slow settling.

Decant off the liquid as closely as possible without dis-

turbing the precipitate (the use of a siphon for this purpose is often advantageous). Add about 250 c.c. of hot water and let the precipitate settle again. Decant this in the same way. Repeat this until the liquid decanted off no longer reacts for HCl with $AgNO_3$.

Should the liquid settle badly as the washing proceeds, add 2 or 3 drops of NH_4OH, which will cause it to clear promptly.

Finally transfer the precipitate of $Al_2O_3 + Fe_2O_3 (+TiO_2 +$ traces of SiO_2) to a filter (do not wash on the filter) and dry. Transfer the precipitate to a crucible, carefully burn the paper *separately*, add the ash to the crucible, ignite strongly and weigh. After weighing, brush the Al_2O_3, etc., out into a small beaker, cover it with a mixture of strong H_2SO_4 8 vols. water 3 vols. and digest on a hot plate for some time. All will dissolve but a slight residue of SiO_2. Dilute the liquid, filter off and weigh this residue and deduct it from the weight of the precipitate first obtained. In the liquid determine the *iron* volumetrically, as in iron ores. Calculate it as Fe_2O_3 and deduct this from the $Al_2O_3 + Fe_2O_3$ and the remainder will be Al_2O_3.

Collect all the washings from the Al_2O_3 except the first, separate from the first liquid decanted off, boil them down rapidly in a large porcelain dish to a small bulk and transfer them to a beaker. Now add a few drops of NH_4OH and filter from any trace of Al_2O_3 separating, using a small ashless filter. Add this filtrate to the first portion which was not boiled down, and the precipitate to the main portion of the Al_2O_3. Now concentrate the total filtrate from the Al^2O_3 to about 200 c.c. on a water bath and determine the CaO and MgO exactly as in the analysis of a limestone.

Determination of the Alkalies by J. Lawrence Smith's Method.

When silicates containing K_2O and Na_2O are heated with a mixture of $CaCO_3$ and NH_4Cl, $CaCl_2$ is first formed by double decom-

position, and this then acts on the silicates forming alkaline chlorides and lime silicates. A red heat is necessary.

There is needed, first pure $CaCO_3$, free from K_2O and Na_2O. This can be prepared by dissolving marble in HCl, to saturation, adding a little slaked lime to make the liquid alkaline and precipitate Fe_2O_3, Al_2O_3 and P_2O_5, then diluting and heating the liquid and precipitating the $CaCO_3$ by $(NH_4)_2CO_3$. This is washed till free from HCl and dried. Second, pure NH_4Cl. This must be powdered and must volatilize without residue at a low red heat.

Process. Mix one gram of clay with one gram of NH_4Cl. Grind them together in a small porcelain mortar. Add eight grams of $CaCO_3$ and mix thoroughly with the clay and NH_4Cl. Put a little pure $CaCO_3$ on the bottom of a large (30 to 50 c.c.) platinum crucible and then add the mixture. Clean out the mortar by grinding a little more $CaCO_3$ in it and add this on top of the mixture as a cover.

Now cover the crucible and heat carefully, gently at first, but gradually to full redness for an hour. Cool and transfer the sintered mass to a casserole. Wash the crucible and cover with hot water and add the washings. Digest the whole until the mass slakes down to a fine powder. Now filter and wash with hot water until the filtrate amounts to 250 c.c.

This amount of washing will take out all the alkali though the filtrate will still react for chlorine, due to the fact that the CaO retains slowly soluble oxychlorides which it is impossible to wash out completely, and which will cause the filtrate to react for chlorine indefinitely.

To the filtrate add NH_4OH and $(NH_4)_2CO_3$ in excess. The calcium separates as carbonate, which on warming becomes granular and easily filtered. Filter and wash with water containing a very little NH_4OH.

Concentrate the filtrate to a small volume, then transfer it to a small porcelain or platinum dish and finally evaporate it to dryness. Now ignite it carefully at a heat not exceeding a barely visible red, until all NH_4Cl is expelled and no more fumes form. Cool, add a little water and a few drops of $(NH_4)_2$

CO_3, and filter from any residue. Add two or three drops of HCl to the filtrate and again evaporate to dryness in a weighed dish. Dry, ignite carefully as before and weigh as KCl + NaCl. The chlorides must be *white* and dissolve without residue in water.

To the water solution add an excess of platinic chloride, and evaporate carefully nearly to dryness. Add 20 c.c. of alcohol (80 per cent.) and let stand till the Na salts dissolve. Filter on to a weighed filter. Wash the K_2PtCl_6 with 80 per cent. alcohol. Dry and weigh. Calculate the K_2O from the weight of this and the Na_2O from the remainder, after deducting the KCl calculated from the K_2O, from the mixed chlorides.

The strength of the alcohol is important. The K_2PtCl_6 is practically insoluble in 80 per cent. alcohol, but the Na_2PtCl_6 will dissolve in it. Time must be given to secure complete solution of this latter salt.

Titanium may be determined in fire clay as in the insoluble residue from titaniferous iron ores.

Clay contains silica as fine sand or quartz, also silica in combination with alumina. It is sometimes desirable to find the amounts of these separately. The quartz is insoluble in potash solution, while the SiO_2 left after evaporation of solutions of silica in HCl is soluble as is also that from the decomposition of silicates by H_2SO_4.

Process for the Determination of Free and Combined Silica. Treat 1 gram of the clay with 10 to 15 c.c. of concentrated H_2SO_4. Heat to near the boiling point of the acid and digest for 12 hours. Cool, dilute, filter, wash and ignite to constant weight.

The residue consists of SiO_2 as sand, SiO_2 from the decomposition of the silicate of alumina together with undecomposed silicates. Transfer to an agate mortar, grind fine, brush on to a watch glass and weigh again.

Heat 50 c.c. of a 15% solution of KOH to boiling in a platinum dish. Add the above weighed residue and boil 5 minutes. Again filter, wash, ignite and weigh. The silica which had been separated from the alumina will have dissolved, the residue being sand and silicates. Deduct this weight (calculated to the whole residue) from the original weight of residue and the difference will be the *combined silica*. This in turn deducted from the total silica, regularly determined, gives the silica in sand and undecomposable silicates.

THE DETERMINATION OF COPPER IN ORES.

Most copper ores are dissolved by digestion with concentrated HNO_3. Sulphur may separate, but will be practically free from copper. Some few bodies (as slags) may require to be fused with sodium carbonate and nitrate.

The most generally reliable method for the determination of copper is by electro-deposition. The conditions most favorable are, a sufficiently dilute solution, not too much free acid, and not too strong a current. Failure in these will cause the copper to be spongy, dark colored and difficult to wash.

Hydrochloric acid must be absent; also much nitric acid. Much arsenic, antimony, bismuth or silver in the solution will cause the copper to be impure. Bismuth is especially troublesome very small percentages causing the results to be high. Should these elements be present in the ores they must be removed before precipitating the copper. They are rarely present in ordinary ores in quantities sufficient to influence the results.

Process for Ordinary Copper Ores. Take an amount of ore which shall not contain more than 0.200 gram of Cu. It must be very finely pulverized. Put it into a small beaker, add 5 c.c. HNO_3, 5 c.c. HCl and 5 c.c. H_2SO_4. Cover with a watch glass and boil until the ore is decomposed, all the HCl and HNO_3 are expelled and white fumes of H_2SO_4 begin to appear. Cool, dilute to 50 c.c. and boil. If silver is present, add one drop of HCl to precipitate it and then filter and wash. The residue should be light colored and must be tested for copper with the blow-pipe.

Put the solution in a weighed platinum dish of 100 c.c. capacity. Connect the dish with the zinc side of a battery of two gravity cells or its equivalent, and introduce into the solution a platinum plate connected with the copper end of the battery. The deposition begins at once and is complete in seven or eight hours. When all trace of blue color is gone from the solution, take a little of the liquid out with a pipette and test it with H_2S water. If no tinge of

CO_3, and filter from any residue. Add two or three drops of HCl to the filtrate and again evaporate to dryness in a weighed dish. Dry, ignite carefully as before and weigh as $KCl + NaCl$. The chlorides must be *white* and dissolve without residue in water.

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brown is produced the Cu is all down. Empty the dish, wash it carefully first with distilled water, then with strong alcohol. Evaporate the alcohol, avoiding a temperature much above 100°C and weigh the dish plus the copper.

The alcohol may be lighted and "burned off" and the heat thus developed will dry the dish. The copper must be red, coherent and metallic. A slight brownish discoloration will not effect the results perceptibly.

If the copper is very dark colored it is impure. Dissolve it carefully in HNO_3 1.2 sp, gr. Evaporate the solution with H_2SO_4 till the HNO_3 is expelled. Filter and re-precipitate it as before.

Instead of precipitating the copper in a platinum crucible as above described, the solution can be put into a beaker and the copper collected on a sheet of platinum foil rolled into a cylinder and connected with the zinc pole of the battery, the other pole being connected with a stout platinum wire running down into the liquid along the axis of the cylinder. This arrangement requires less platinum and is very convenient where a sufficient number of determinations are made to warrant the expense of special apparatus. In this case if the copper deposit is dark and impure it can frequently be purified by reversing the current until the copper is dissolved and then re-precipitating in the same solution. The impurities do not readily dissolve but loosen and fall to the bottom of the beaker and the second copper deposit is pure.

For further detail consult Peter's "American Method of Copper Smelting," and also "A Manual of Practical Assaying," by H. Van F. Furman.

THE IODINE METHOD FOR COPPER.

This depends on the fact that when a cupric salt is treated with potassium iodide, cuprous iodide is formed and iodine liberated. The iodine is then estimated volumetrically with sodium thiosulphate. The solution must be slightly acid and must not contain any large amount of sodium acetate. Iron must be absent. Bismuth causes some uncertainty by making it difficult to see the end reaction owing to the formation of brown bismuth iodide, but with practice this can be overcome.

Preparation of the Thiosulphate Solution. Dissolve 39.18 grams crystallized sodium thiosulphate in water and dilute to one liter. 1 c.c. should equal 0.01 gram of copper.

The reactions from which this is calculated are as follows: $CuSO_4$

$+2\,KI=CuI+I+K_2SO_4$ and $2\,Na_2S_2O_3\,5H_2O+2\,I=2NaI+Na_2S_4O_6$ $+5H_2O$. Standardise the solution against pure copper. Dissolve the copper in 5 c.c. of dilute nitric acid (1 to 1), boil off all nitrous fumes (this is essential as they would liberate iodine) dilute with an equal bulk of water and add a solution of NaOH cautiously until a permanent precipitate is just produced. Now add 1 c.c. of acetic acid, which must give a clear solution. *If the liquid is warm cool it.* Now add 3 grams of pure potassium iodide. When it is dissolved dilute to 100 c.c. Now run the thio solution from a burette until the brown color due to the liberated iodine is nearly discharged. Then add 2 or 3 c.c. of starch solution and continue the titration until the blue color disappears and *does not return on standing four minutes.* The number of c.c. used will be equivalent to the copper taken.

Process for Ores. Heat 2 grams of the ore in a small covered beaker or casserole with 20 c.c. of concentrated HNO_3. When violent action has ceased boil down to dryness. Take up with 30 c.c. of concentrated HCl, digest and dilute to 200 c.c. without filtering. Warm and pass a rapid current of H_2S through the solution till the Cu is all down as sulphide. Filter and wash with water containing a little H_2S. Wash the precipitate back into the beaker or dish. If more than a trace remains on the filter, burn it and add the ash to the rest. Now add 15 c.c. of concentrated HNO_3 and boil almost to dryness. Add 20 c.c. of water and boil till all nitrous fumes are expelled. Filter from the gangue and sulphur. Neutralize the solution with NaOH solution and add acetic acid as in standardizing. Cool it and add 5 grams of KI, dilute to 100 c.c. and titrate with the thiosulphate solution. The filter should be burned in a porcelain crucible and the residue examined for copper.

See "A Text Book of Assaying," C. and J. J. Beringer.

Sheet aluminum can be used instead of H_2S for separating the copper. Evaporate the HCl solution with 5 c.c. of concentrated H_2SO_4 until the HCl is expelled and H_2SO_4 fumes appear. Cool, add 20 c.c. of water and boil to effect complete solution. Dilute to about 50 c.c. and put about four square inches of sheet aluminum into the liquid. Add 5 c.c. more of H_2SO_4 and boil till the Cu is all down. Wash the precipitated Cu by decantation and dissolve in 5 c.c. of HNO_3 sp. gr. 1.2.

This will not attack the aluminum but will dissolve the Cu completely. Filter off the solution and proceed as usual. See Low, Jour. Am. Chem. Soc. 1896. p. 358.

THE CYANIDE ASSAY FOR COPPER ORES.

This method gives good results if exactly followed. It depends upon the fact that if a solution of KCN is added to the blue solution of a copper salt in excess of NH_4OH the blue is discharged owing to the formation of a colorless double salt. The amount of cyanide required in the titration is affected by the volume of the liquid, the amounts of ammonia and of ammonium salts present, and to a slight extent by the temperature of the solution.

The method given by Low is as follows :

Standard Cyanide Solution.—Dissolve about 42 grams of pure KCN in 1 litre of water. This will give a solution of which 1 c. c. is approximately equivalent to 0.01 gram of copper. To standardize the solution, dissolve 0.2 gram of pure copper in 5 c.c. of concentrated HNO_3. Boil off the red fumes and dilute to about 125 c.c. Cool and add 10 c.c. of strong NH_4OH. Run in the KCN solution till the color is nearly discharged. Now dilute to 180 c.c. and finish the titration. The end is marked by the complete disappearance of the blue color.

Assay of the Ore.—Treat one gram with 7 c.c. of concentrated HNO_3, 5 c.c. of H_2SO_4 and 2 c.c. of HCl in a 250 c.c. Erlenmeyer flask. Boil down till H_2SO_4 only remains and white fumes appear. Cool, add 10 c.c. of water, boil till ferric salts are dissolved; again cool and add 6 grams of pure granulated zinc. Shake the mixture for five minutes, dilute to 50 c.c. and add 20 c.c. of H_2SO_4. As soon as all the zinc is dissolved, fill the flask with water, let the Cu settle completely and decant off the liquid. Wash in this way at least twice. The liquid decanted off should be tested for copper with H_2S. If it shows any repeat the assay or filter off the CuS and determine it. Add 5 c.c. of concentrated HNO_3 to the residue in the flask, and boil till the Cu is dissolved and the red fumes expelled. Now dilute the solution to 125 c.c.

If silver is present, add a drop of HCl to precipitate it. If more than a trace separates, filter it off or it will count as copper in the titration. Now add 10 c.c. of strong NH_4OH and run in the KCN solution until the color is nearly discharged. Pour the solution on a large ribbed filter and let it all run through. Dilute the filtrate to 180 c.c. and finish the titration. As it should only take a very little of the cyanide solution to finish the titration in the filtrate, the little required by the Cu left with the insoluble residue and oxide of iron in the filter can be disregarded.

If only an approximate determination of the Cu is desired, it can be made very rapidly by omitting the zinc precipitation. In this case treat one gram of the ore with 5 c.c. concentrated HNO_3, and boil till the Cu is extracted and most of the acid driven off. Now add 5 c.c. more HNO_3, dilute to 125 c.c., add 10 c.c. of strong NH_4OH and run in the cyanide till the blue color is nearly discharged. Filter off and finish the titration as before. If there is a very large precipitate of Fe $(OH)_3$, repeat the process on a new sample of ore, adding nearly sufficient cyanide solution as calculated from the first determination before filtering.

THE ASSAY OF ORES FOR ZINC.

Zinc usually occurs in ores as sulphide, oxide, carbonate or hydro-silicate. All of these are decomposed by boiling with acids, the zinc passing into solution. When sulphur is present it can be oxidized by HNO_3 and $KClO_3$.

Solutions of zinc in HCl are completely precipitated by potassium ferrocyanide. Iron, copper, cadmium and manganese are also precipitated in the same way, and if present must be removed from the solution before the zinc is determined.

An excess of ferrocyanide in the solution can be recognized by the brown precipitate (uranic ferrocyanide) it gives with a solution of uranic nitrate or acetate. This reaction is less sharp in acid solution, but by using a concentrated solution of the uranium salt, and only a little of the solution to be tested, is still sufficiently delicate.

The HCl solution must be free from Cl or oxides of chlorine, as these decompose the ferrocyanide and liberate iron salts.

PROCESS OF VON SCHULZ AND LOW.

Solution of the Ore and Separation of the Fe, Mn and Cu. Weigh one gram into a 4-inch casserole. Add 2 or 3 c.c. of concentrated HNO_3, then cautiously 25 c.c. of HNO_3, previously saturated with $KClO_3$ by shaking up with crystals of the salt. (Keep this solution in an open bottle.) When the violent action is over, cover the casserole and boil rapidly to dryness. Do not bake the residue. Now cool and add seven grams of NH_4Cl, 25 c.c. of hot water and 15 c.c. of strong NH_4OH. Boil the liquid one minute and then rub the dish with a rubber tipped rod to loosen and disintegrate all the insoluble matter. Filter and wash several times with a boiling hot 1 per cent. solution of NH_4Cl. If the filtrate is *blue* Cu is present.

Add to the filtrate 25 c.c. of concentrated HCl and dilute to 200 c.c. If Cu is present add forty grams of "granulated lead" and stir until the liquid is colorless.

Strips of aluminum foil may be substituted for the lead. These

strips can be cleaned from copper with dilute HNO_3, and can be used repeatedly (Furman).

The zinc salts are soluble in NH_4OH, while the $Fe(OH)_3$ and $Al(OH)_3$ are precipitated. When much zinc is present or much iron, the residue may retain enough to affect the results 1 or 2 per cent. In this case it must be dissolved in a little HCl, and reprecipitated by NH_4OH.

This second filtrate will contain Mn if present in the ore. To remove it add 5 or 10 c.c. of hydrogen peroxide and filter from the MnO_2. Add this filtrate to that from the main quantity.

The HNO_3 and $KClO_3$ separate all the Mn in the first case as MnO_2, but this dissolves in the HCl again.

It is essential that all the $KClO_3$ be decomposed and the Cl driven off in the evaporation, as if any is present in the final solution for titration it will cause the solution to become greenish blue on the addition of ferrocyanide and make the results high. This may be prevented by somewhat more prolonged heating of the dry residue until all $KClO_3$ is decomposed, or by adding a little *sodium sulphite* to the solution before titration.

The granulated lead precipitates the Cu as metal. The lead in solution does not interfere with the subsequent titration.

Volumetric Determination of the Zinc—Preparation of the Ferrocyanide Solution. Dissolve 44 grams of pure $K_4Fe(CN)_6$ $3H_2O$ in water and dilute to one litre. 1 c.c. of this will precipitate approximately 0.01 gram of Zn.

Standardize the solution against pure zinc. Dissolve 0.2 gram in 10 c.c. of HCl, add 7 grams of NH_4Cl, dilute to 100 c.c. and heat to about 50°C. Now run in the ferrocyanide solution until a drop of the liquid shows a brown tinge when tested on a white plate with a drop of a strong solution of uranic nitrate after standing two or three minutes. To save time add nearly the correct amont of the solution and then add about 1 c.c. $\frac{1}{10}$ c.c. at a time, making a test after each addition but not waiting for the color to develop. Let the series stand and take as the end the test showing the color after three minutes. Now make a similar test upon the $HCl + NH_4Cl$ without the zinc. Deduct the amount of this "blank" from the other, and the difference gives the amount of the solution, equivalent to 0.2 gram zinc.

Determination of the Zinc. Titrate the strongly acid solution of the ore exactly as above. The liquid should be warmed to about 50° before titration.

The precipitate must be pure white. If it is at all green, iron chlorous acid is present, and the results will be too high.

To avoid "running over" it is a good plan to take out one-third the liquid. Titrate the remainder roughly, and then add the one-thi and finish carefully.

Cadmium when present counts as zinc in this process.

See Jour. An. and App. Chem., vol. VI, p. 491.

Beringer, Assaying.

Hinman, S. of M. Quarterly, 1892, p. 40.

THE ANALYSIS OF ALLOYS OF LEAD, ANTIMONY, TIN AND COPPER. (BEARING METAL.)

Traces of As, Fe and Zn are often present. The complete analysis of these alloys is beyond the scope of these notes, but the following method for the determination of the four principal metals will be found satisfactory if carefully conducted.

The most troublesome operations are the separation of the tin from the lead and from the antimony.

See Fresenius Quantitative Analysis, § 164, also § 165, § 126 and § 125.

Process. Weigh 0.5 gram of the fine shavings into a 150 c.c. beaker. Add 2 grams of solid tartaric acid (powdered), and then 15 c.c. of HNO_3, 1.2 sp. gr. Cover and warm until everything is dissolved, wash off and remove the cover and evaporate carefully to a pasty mass. Now add 50 c.c. of water and warm until all the lead nitrate has dissolved. The oxides of tin and antimony, in part, are left as a fine white powder. Now drop in a concentrated solution of KOH until the precipitate formed is dissolved in the excess. A cloudiness may remain, but almost all will go into solution. Add 10 c.c. of yellow sodium sulphide ₁ and digest at a temperature considerably short of boiling for three or four hours, stirring occasionally and keeping the beaker covered. Now decant the clear liquid through a filter, and wash once by decantation. Avoid getting the precipitate on the filter, but decant closely each time. To the residue add 10 c.c. more of the sulphide solution, but no water, and digest again for two hours. Then add 50 c.c. of water and warm, let settle, decant, transfer and wash the precipitate with H_2S water.

The Precipitate contains PbS and CuS. Dry the filter and precipitate. Detach the latter as completely as possible and burn the filter in a small porcelain crucible using a very low heat and merely driving off volatile matter, not attempting to completely burn the carbon. Now add the burned filter to the rest of the PbS in a small casserole. Cover and add a few drops of concentrated HNO_3 to moisten the PbS; then add 5 c.c. of *fuming* HNO_3 (1.5 sp. gr.). Warm for some time and, when all sulphur has disappeared, add 5 c.c. of H_2SO_4 (1:3) and evaporate till all HNO_3 is expelled. Now add 25 c.c. of water, stir well, let settle, filter and wash with water containing 1 per cent. H_2SO_4, and finally wash with alcohol. The precipitate is $PbSO_4$. When it is dry, detach it carefully from the filter and put in a small weighed porcelain crucible. Burn the filter paper carefully on the inverted lid of the crucible and

1. *Sodium Sulphide Solution.* This is made by saturating a 20 per cent. solution of sodium hydrate with H_2S gas. Then filter the solution and add to each 100 c.c. about 100 milligrams of flowers of sulphur. This will dissolve and make the liquid yellow. This solution must be kept in filled, closely stopped bottles.

add to the ash one or two drops of concentrated HNO_3 and one drop of H_2SO_4, evaporate off the acids carefully, and finally dry and ignite the crucible and cover at a low red heat. Now weigh all together and calculate the Pb from the weight of the $PbSO_4$.

The filtrate from the $PbSO_4$ contains the Cu. This may be precipitated by the battery, or it may be thrown down by a current of H_2S, filtered out, washed with H_2S water, dried, ignited and weighed as $CuO + Cu_2S$. (The fact that the precipitate is partially converted to oxide by the air is unimportant, as the percentage of Cu in CuO and Cu_2S is the same.)

The Filtrate from the PbS and CuS contains the Sb and Sn (and As) as sulphides. Dilute the liquid to about 250 c.c. Add HCl carefully until the solution distinctly reddens litmus, but avoid much excess, set on a warm plate and heat *gently* until the odor of H_2S has nearly gone.

Filter and wash once by decantation, then run the precipitate on to the filter. The filtrate will grow milky in time, but no precipitate should separate from it.

The precipitate, consisting of Sb_2S_3, SnS_2 and free sulphur, is now washed back into the beaker, using a wash bottle with a small jet, so as to accomplish this with but little water. With care the amount of precipitate left on the filter paper will be but trifling. Now dissolve this off *through the filter* into the beaker with a few drops of a dilute solution of NaOH. The liquid in the beaker need not be more than 75 c.c. Add to the contents (water and sulphides) 10 to 15 grams of solid NaOH. When this is dissolved, add carefully about 3 c.c. of *bromine* (not "bromine water"). Now digest on a water bath keeping the beaker covered, until the sulphur is oxidized or collected in a granular form and the antimony has separated as a white crystalline precipitate of sodium metantimoniate.

Test the liquid by adding a drop or two of HCl to a drop of it, if *bromine vapor* is given off enough Br has been added. Add a little more if needed. Finally boil the liquid a few minutes. Now cool and add one-third the volume of alcohol. Let stand some hours, filter and wash with water containing one-third its volume of alcohol and a little Na_2CO_3. The filtrate contains all the SnO_2 as sodium stannate, and the precipitate contains the antimony and often some free sulphur.

Dilute the *filtrate* to 200 c.c., add HCl until it is distinctly acid, and warm till the Br is expelled. Then add 200 c.c. of H_2S water, and pass in H_2S gas till saturated. Let stand till the precipitate settles, filter and wash the SnS_2 thoroughly. If the precipitate tends to run through the filter, add ammonium acetate to the wash water. Put the filter and precipitate in a weighed porcelain crucible, dry and burn off the paper very carefully, finally ignite and weigh as SnO_2. Add a little solid am-

monium carbonate to the crucible; heat, ignite intensely and weigh again. Any loss is due to sulphuric acid held by the SnO_2.

The Antimony Precipitate is washed back into the beaker and dissolved in the least possible amount of dilute HCl, containing a little tartaric acid. Wash the filter with the same, and finally filter the solution from any residual sulphur. (This will be free from antimony.)

Now dilute to about 250 c.c., heat nearly to boiling and pass in a rapid current of H_2S till the Sb_2S_3 is all precipitated.

Weigh a 7 cm. filter paper, as in the phosphorus determination by the yellow precipitate method. Let the Sb_2S_3 precipitate settle, decant through the filter. Transfer the precipitate, wash well and dry carefully at 100°C and weigh filter, plus precipitate. This gives the total weight of the precipitate, which always contains free sulphur. Now detach as much as possible from the filter paper, transfer it to a weighed porcelain boat and weigh the boat and contents.

Take a piece of combustion tubing wide enough to receive the boat and its contents and ten or twelve inches long. Connect one end with a flask for generating CO_2 from fragments of marble. Close the other end of the combustion tube with a cork containing a small exit tube. (There must be a U-tube containing $CaCl_2$ between the flask and the combustion tube to remove moisture from the gas.)

Now put the boat and its contents into the middle of the tube, pour a little dilute HNO_3 into the CO_2 flask and let the current of gas pass till all air is expelled (four or five minutes). Now carefully heat the tube around the boat. The free sulphur volatilizes and the Sb_2S_3 turns black and metallic looking. When this change is complete and no more sulphur vapors pass off, cool the apparatus, withdraw the boat and weigh it. The weight of the contents gives the pure Sb_2S_3 in the amount taken. From this calculate the Sb_2S_3 in the total precipitate as weighed originally, and from this again the Sb in the sample.

Notes on the Above Scheme. The use of the tartaric acid is to assist in the solution of antimony, which is but slowly oxidized by HNO_3 alone. The separation of tin by the solubility of the bisulphide in sodium sulphide is complete, provided there is repeated and prolonged digestion with large excess. Sulphide of sodium is used instead of sulphide of ammonium as the latter dissolves copper sulphide. In the treatment of the PbS the use of the fuming nitric acid causes the complete oxidation of the sulphur. With ordinary concentrated nitric acid, which contains about 30% of water, more or less sulphur separates which fuses into globules. When the $PbSO_4$ is ignited this melts and causes reduction to sulphide, and loss of weight.

The fuming acid can be most easily prepared by mixing in a large retort one part of ordinary HNO_3 with two parts of concentrated

H_2SO_4 and distilling off the nitric acid into a cooled dry receiver. The neck of the retort should project well into the receiver.

Arsenic, if present, is found with the stannic sulphide. It is driven off on heating the SnO_2.

The foregoing method for the separation of tin and antimony depends upon the oxidation of the Sb_2S_3 by the sodium hypobromite to sulphuric acid and sodium metantimoniate. The usual method of effecting this is by fusion with sodium hydrate and nitrate, after preliminary oxidation by HNO_3. The wet method above given is much less troublesome and equally complete.

The above method while long, will give satisfactory results.

The lead may also be separated as chloride and determined as chromate. Tin may be separated from antimony and arsenic by oxalic acid, which dissolves the sulphide of tin (Clark's method.) The tin may be determined electrolytically in this solution. Antimony may be determined by titrating the solution of the chloride obtained by oxidizing the sulphide with HCl and $KClO_3$. On adding an excess of KI to a solution containing the $SbCl_5$ iodine is liberated, the solution reducing the $SbCl_3$. The iodine can then be determined with $Na_2S_2O_3$. Arsenic can be estimated by distillation with HCl and ferrous chloride as in iron. Tin may be titrated with iodine which changes $SnCl_2$ to $SnCl_4$. Iron does not interfere if the solution is kept ice cold, and the tin solution is introduced under an excess of the iodine solution. For full accounts of these methods see

Mason, Jour. Soc. Chem. Ind., 1896, p. 179.

Lenssen, Jour. für. Praktische Chem., 78:200. Also Fresenius Quantitative Analysis and Muller. Chem. News, Mar. 7, 1902.

Clark, Am. Jour. Sci., vol. XLIX, p. 154 and Am. Chem. Jour., vol. I, p. 244.

THE EXAMINATION OF WATER FOR BOILER SUPPL|

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Third. Acidulate one litre with 5 c.c. of HCl, evaporate to dryne
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For ordinary work where the amount of SiO_2 is usually very triflir
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THE EXAMINATION OF WATER FOR BOILER SUPPLY.

The determination of the "scale-forming ingredients" and in the case of water contaminated with mine drainage, the "acidity" of the water is all that is necessary.

Outline Process for the Analysis.—First, evaporate 100 c.c. of the clear water (filtered if necessary) to dryness in a weighed platinum dish, and dry at 100° to constant weight. This gives the "total solids." After weighing the dish ignite it very cautiously, not passing a barely visible red heat, until the residue becomes nearly white. Weigh again after cooling in a desiccator. The loss is water of combination and organic matter, and the residue is the fixed mineral matter.

Second. Test the water for chlorine. If it contains more than a trace, the amount may be determined by titrating 100 c.c. of the water with a standard solution of $AgNO_3$, adding a little neutral potassium chromate to serve as an indicator. A slight excess of $AgNO_3$ gives the reddish color of silver chromate (See Fresenius Quantitative Analysis.)

The small excess of the silver solution required to give the red color that forms the end reaction, can be determined by adding 1 c.c. of a standard solution of NaCl (1 c.c. equal 1 milligram Cl) to 100 c.c. of distilled water, and titrating this in the same way. The excess of the silver solution over that required for the chlorine present, is the amount that must be deducted from that used in the regular titration.

Third. Acidulate one litre with 5 c.c. of HCl, evaporate to dryness in a platinum dish, adding it to the dish little at a time. Take up the residue with HCl and water, and determine the SiO_2, Fe_2O_3 and Al_2O_3, CaO and MgO exactly as in the case of limestone. In filtering off the SiO_2 care must be taken that no $CaSO_4$ (which is frequently present in considerable quantity) be left undissolved with the SiO_2. It can all be dissolved with water and HCl.

For ordinary work where the amount of SiO_2 is usually very trifling and of no technical importance, the evaporation to dryness can be omitted. In this case evaporate one litre of the water with 5 c.c. of HCl in a large beaker, to about 100 c.c. Add an excess of NH_4OH and filter from the precipitate of $Fe_2(OH)_3$, $Al_2(OH)_3$ and SiO_2. Care must be taken to have enough HCl present to prevent any precipitation of the magnesia. The CaO and MgO are determined in the filtrate as before.

Fourth. Acidulate 500 c.c. of the water with 1 c.c. of HCl and evaporate to 100 c.c. Filter if necessary, and determine the SO_3 by precipitation with $BaCl_2$.

The alkalies may be determined closely enough for technical purposes by difference as follows:

Evaporate 100 c.c. to dryness with a slight excess of H_2SO_4 in a weighed platinum dish. Ignite the residue cautiously till the fumes of H_2SO_4 are all driven off; do not exceed a low red heat. Now put a few small pieces of pure $(NH_4)_2CO_3$ into the dish, and cautiously heat till it is evaporated. This will expel the acid retained by the alkalies, to form bisulphates. Avoid too much heat or $MgSO_4$ will be decomposed. Now cool and weigh the dish which contains the sulphates of all the bases in the water. Calculate the CaO and MgO as sulphates, add the Fe_2O_3, Al_2O_3 and SiO_2, and deduct the sum from the weight of the sulphates in the dish. The difference may be taken as sodium sulphate.

If a more exact determination of the alkalis is needed, evaporate one or two litres of the water to dryness in a platinum dish. Glass is liable to give up alkali. Extract the residue with water, add an excess of pure milk of lime, digest and filter, and proceed with the solution as with the filtrate from the lime in the determination of alkalies in the Analysis of Fire Clay. A blank must be run on all the reagents. In place of using a platinum dish the water may be boiled down to dryness in a clean tin sauce pan, and the residue used for the determination of the alkalies. This will be found a useful method where a number of waters are to be analyzed and the supply of platinum ware is short.

Calculation of the Results.—In stating the results of the analysis it is customary to combine the acids and the bases in the following manner: The alkalies are first combined with the chlorine any excess being then combined with the sulphuric acid. Should there be more chlorine than will combine with the alkalies the excess is calculated first to the calcium and when that is used up, to the magnesium. Should there be alkalies more than sufficient to saturate both the chlorine and the sulphuric acid the excess is estimated as carbonate.

The sulphuric acid left after the alkalies are satisfied is then united with the calcium and any excess combined with the magnesium.

All the calcium and magnesium not required for the chlorine and the sulphuric acid are then calculated as carbonates.

This order can be departed from where there is evidence of some other combination. In water that has been treated with lime and soda to remove the lime, magnesia is frequently present as hydroxide. In estimating the effect of the magnesia compounds in causing corrosion in boilers all the chlorine and the sulphuric acid in excess of that required to saturate the alkalies should be considered as combined with the magnesia. The table in the end of the book will be found useful in making these calculations.

The analysis should be reported in parts per million and in grains per gallon.

TABLE OF ATOMIC WEIGHTS.

Aluminum	Al	27.1	Neodymium	Nd	143.6
Antimony	Sb	120.	Neon	Ne	20.
Argon	A	39.9	Nickel	Ni	58.7
Arsenic	As	75.	Niobium	Nb	94.
Barium	Ba	137.4	Nitrogen	N	14.04
Beryllium	Be	9.1	Osmium	Os	191.
Bismuth	Bi	208.5	Oxygen	O	16.
Boron	B	11.	Palladium	Pd	106.
Bromine	Br	79.96	Phosphorus	P	31.
Cadmium	Cd	112.4	Platinum	Pt	194.8
Caesium	Cs	133.	Potassium	K	39.15
Calcium	Ca	40.	Praseodymium	Pr	140.5
Carbon	C	12.	Rhodium	Rh	103.
Cerium	Ce	140.	Rubidium	Rb	85.4
Chlorine	Cl	35.45	Ruthenium	Ru	101.7
Chromium	Cr	52.1	Samarium	Sa	150.
Cobalt	Co	59.	Scandium	Sc	44.1
Copper	Cu	63.6	Selenium	Se	79.1
Erbium	Er	166.	Silicon	Si	28.4
Fluorine	F	19.	Silver	Ag	107.93
Gadolinium	Gd	156.	Sodium	Na	23.05
Gallium	Ga	70.	Strontium	Sr	87.6
Germanium	Ge	72.	Sulphur	S	32.06
Gold	Au	197.2	Tantalum	Ta	183.
Helium	He	4.	Tellurium	Te	127.
Hydrogen	H	1.01	Thallium	Tl	204.1
Indium	In	114.	Thorium	Th	232.5
Iodine	I	126.85	Thulium	Tu	171.
Iridium	Ir	193.	Tin	Sn	118.5
Iron	Fe	56.	Titanium	Ti	48.1
Krypton	Kr	81.8	Tungsten	W	184.
Lanthanum	La	138.	Uranium	U	239.5
Lead	Pb	206.9	Vanadium	V	51.2
Lithium	Li	7.03	Xenon	Xe	128.
Magnesium	Mg	24.36	Ytterbium	Yb	173.
Manganese	Mn	55.	Yttrium	Y	89.
Mercury	Hg	200.3	Zinc	Zn	65.4
Molybdenum	Mo	96.	Zirconium	Zr	90.7

TABLE OF FACTOR WEIGHTS.

By taking for analysis the weights of material given in the following table, each milligram of the substance weighed will represent the indicated percentage of the substance sought.

Substance to be Determined	Substance to be Weighed	Factor	Factor Weight to be Taken	Percentage Represented by 1 Milligram
S	$BaSO_4$	0.1373	1.373	0.01
SO_3	$BaSO_4$	0.3433	0.687	0.05
Si	SiO_2	0.4702	0.9404	0.05
P	$Mg_2P_2O_7$	0.2790	2.790	0.01
P_2O_5	$Mg_2P_2O_7$	0.6396	*2.130	0.03
Mn	Mn_3O_4	0.7200	1.440	0.05
Mn	$Mn_2P_2O_7$	0.3873	0.387	0.10
C	CO_2	0.2727	2.727	0.01

* The factor multiplied by $\frac{10}{3}$

USEFUL CONSTANTS.

1 Gram = 15.43236 Grains.   Log. = 1.18843.

1 Gallon = 231 Cubic inches. = 3.78543 Litres.   Log. = 0.57811.

1 Litre = 1.0567 Quarts.   Log. = 0.03369.

1 Litre = 0.26417 Gallons.   Log. = 9.42188.

1 Litre = 61.023 Cubic inches.   Log. = 1.78549.

The grain troy is the same as the grain avoirdupois. The U. S. avoirdupois pound is 7000. grains, equals 453.59 grams.   Log. 2.65666

The U. S. gallon of water, measured at 4°C and under atmospheric pressure weighs 58353. grains.   To convert parts per million to grains per gallon multiply by 0.058353.   Log. = 8.76606—10.

TABLE OF USEFUL FACTORS FOR WATER ANALYSIS.

Given	Required	Factor	Logarithm
K_2O	2 KCl	1.582	0.19926
K_2O	K_2SO_4	1.849	0.26694
KCl	Cl	0.475	9.67688
2 KCl	K_2SO_4	1.169	0.06768
K_2SO_4	SO_3	0.459	9.66197
K_2PtCl_6	2 KCl	0.307	9.48731
K_2PtCl_6	K_2O	0.194	9.28805
Na_2SO_4	Na_2CO_3	0.746	9.87294
Na_2SO_4	SO_3	0.563	9.75064
Na_2O	Na_2CO_3	1.709	0.23263
Na_2O	Na_2SO_4	2.289	0.35969
Na_2O	2 NaCl	1.884	0.27510
2 NaCl	Na_2SO_4	1.215	0.08459
2 NaCl	SO_3	0.684	9.83523
$CaSO_4$	$CaCO_3$	0.735	9.86627
$CaSO_4$	CaO	0.412	9.61446
CaO	$CaCl_2$	1.980	0.29674
CaO	$CaCO_3$	1.786	0.25181
$BaSO_4$	SO_3	0.343	9.53521
$BaSO_4$	BaO	0.657	9.81762
$SrSO_4$	SO_3	0.436	9.63941
$SrSO_4$	SrO	0.564	9.75135
$Mg_2P_2O_7$	2 MgO	0.362	9.55922
$Mg_2P_2O_7$	2 $MgCO_3$	0.758	9.87942
$Mg_2P_2O_7$	2 $MgSO_4$	1.081	0.03397
$Mg_2P_2O_7$	P_2O_5	0.638	9.80453
MgO	$MgCO_3$	2.090	0.32019
MgO	$MgCl_2$	2.360	0.37296
MgO	MgO_2H_2	1.447	0.16031
MgO	2 Cl	1.757	0.24470
MgO	$MgSO_4$	2.984	0.47475
$MgCO_3$	$MgSO_4$	1.427	0.15456
SO_3	K_2SO_4	2.178	0.33803
SO_3	$CaSO_4$	1.700	0.23031
SO_3	CaO	0.700	9.84477
SO_3	$MgSO_4$	1.504	0.17728
SO_3	Na_2SO_4	1.776	0.24936
Cl	NaCl	1.650	0.21754
2 Cl	$CaCl_2$	1.564	0.19428
2 Cl	$MgCl_2$	1.344	0.12826
Cl	KCl	2.104	0.32312
AgCl	Cl	0.247	9.39313

N	0	1	2	3	4	5	6	7	8	9	d
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	41
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	38
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	35
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	32
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	30
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	28
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	26
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	25
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	24
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	22
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	21
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	20
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	19
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	18
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	18
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	17
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	16
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	16
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	15
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	15
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	14
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	14
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	13
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	13
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	13
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	12
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	12
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	12
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	11
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	11
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	11
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	10
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	10
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	10
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	10
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	10
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	9
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	9
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	9
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	9
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	8
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	8
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	8
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	8
N	0	1	2	3	4	5	6	7	8	9	d

N	0	1	2	3	4	5	6	7	8	9	d
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	8
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	8
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	8
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	7
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	7
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	7
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	7
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	7
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	7
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	7
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	6
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	6
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	6
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	6
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	6
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	6
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	6
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	6
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	5
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	5
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	5
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	5
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	5
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	5
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	5
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	5
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	5
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	4
100	0000	0004	0009	0013	0017	0022	0026	0030	0035	0039	4

NOTE ON THE BICHROMATE IRON ASSAY.

When stannous chloride is used to reduce ferric salts in the assay of iron ores it is important that no platinum be present in the solution as platinum salts are reduced to the platinous state and then color the liquid an intense yellow making it impossible to destinguish the point at which the iron is reduced. This condition is likely to occur when the ore or residue has been fused in order to bring it into solution, platinum being dissolved from the crucible.

SPECIAL METHOD FOR SULPHUR IN PIG IRON.

The following method was furnished to the writer from Dr. Dudley's laboratory at Altoona.

Into a half litre Erlenmeyer flask put 350 c.c. of a sulution of double chloride of copper and potassium. (Use a filtered solution of 10 pounds of the commercial article in 13 litres of water.) Add 10 c.c. of concentrated HCl to the solution in the flask. Connect the flask with a source of CO_2 and pass the gas through until the air is all expelled, which takes about 15 minutes. Meanwhile heat the flask until it is perceptibly warm to the hand. Now take out the stopper of the flask and drop in five grams of pig iron. The iron should be in a fine state of division and wrapped in a piece of filter paper. Replace the cork and agitate the flask to scatter the borings through the flask. Continue to pass the gas until the iron is dissolved; this takes about half an hour.

When solution is complete filter through paper and wash with 1 per cent. HCl hot. Put the filter and its contents back into the flask. Add 15 c.c. of water 2 c.c of liquid bromine and 5 c.c. of HCl. Heat till the bromine passes off.

Filter from the residue and precipitate hot with $BaCl_2$. The residue is practically free from sulphur rarely retaining more than .001 to .003 per cent.

Several flasks can be connected together.

The CO_2 sold in cylinders can be used for this process.